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**SPECIAL ADVANCED STUDIES FOR  
POLLUTION PREVENTION**

**Delivery Order 0046: Advanced Studies in  
Pollution Prevention Chrome Replacements for  
Internal and Small Parts**



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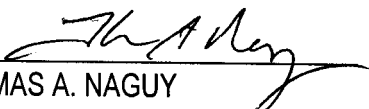
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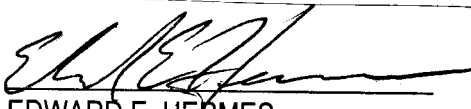
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## Executive Summary

This document is a Technology Analysis assessing the current state of the art in coatings and surface treatments that could be used to replace hard chrome plating on internal diameters (IDs) and heat-sensitive aircraft components. Its purpose is to determine which technologies and materials are viable options for the Joint Strike Fighter (JSF), and estimate what developments will be needed to bring these options to production at original equipment manufacturers (OEMs) and overhaul and repair (O&R) sites, most of which are military depots. The analysis included assessment of written information, including scientific and technical data and trade literature, combined with extensive discussions with manufacturing engineers, development engineers and scientists, depot personnel, and equipment and service providers.

In the Part A we summarize how hard chrome is currently used on aircraft components, illustrating with components that are typical of ID usage. In Part B we outline the most important criteria for hard chrome replacement in both the OEM and O&R environments, the most critical of which is an O&R ability to strip and rebuild worn components. We summarize the technologies we have considered, showing which ones are most likely to fit the criteria in the short (2 year), intermediate (3-5 year), and long term (>5 year). Part C provides details of each of the technologies we have considered, which include

- thermal spray (including HVOF, plasma, nanoparticle)
- electroplating and electroless plating (including alloys and composites)
- chemical and physical vapor deposition (including plasma and combustion CVD, and sputtering)
- laser processing (including laser cladding and alloying)
- weld coating (including micro-arc deposition and explosive cladding)
- heat treatment and ion implantation (including gas and plasma nitriding and carburizing, and beam and plasma source implantation).

We conclude that the only method that is fully developed and **available immediately** is electroless nickel and its composites. However, since Ni, like Cr, is on the EPA-17 toxic substances list, this method is not recommended, except as a stopgap measure.

For the **short term**, alloy plating and Co-composite plating are both possible options. These methods are the closest drop-ins for existing hard chrome plating. However, most of the commonly-used electroplated alloys are Ni-based, and composites pose quite severe uniformity and handling problems, especially in the O&R environment. The **better** (cleaner and higher performance) solution in the short term, we believe, is a combination of plasma spray and electrospray deposition, both of which can be used to deposit WC-Co, the material of choice for OD chrome replacement. This combination should solve almost all existing usage, except landing gear main cylinder IDs.

This shortfall can be solved in the **intermediate term** by the use of small and nanoparticle spray methods, which should allow plasma spray to meet all the criteria for both OEM and O&R use. A second intermediate term solution is ID sputter coating, provided that the coating materials useful for rebuild have adequate properties, the method can be adapted to existing IVD equipment in use at OEMs and depots, and the deposition rates and costs are reasonable.

In the **long term** two CVD methods have promise - combustion CVD and plasma CVD - but it is not clear at this point that the materials that could be deposited by these methods will meet the requirements for component rebuilding.

## **Acknowledgements**

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## **PART A - HARD CHROME USAGE**

In this section we give an overview of current chrome usage, including examples of typical components that currently use ID chrome plating.

# **1. Introduction**

Hard chrome plating is presently used throughout the aerospace industry. At the original equipment manufacturer (OEM) level, usage is primarily for wear resistance, some corrosion resistance, and accurate sizing of components. For IDs, thin dense chrome is frequently used for wear and corrosion resistance, especially in landing gear. At the overhaul and repair (O&R) level the primary use of hard chrome is to rebuild worn components, on both ODs and IDs. The environmental problems of chrome lie primarily in hexavalent chrome air emissions from plating tanks. Secondly, chrome-contaminated waste must be cleaned up before discharge, making rinse water and chrome stripping a secondary source of pollution at military depots.

High Velocity Oxy-Fuel thermal spray (HVOF) has been used in aircraft engines for some years. The method is now being adopted widely in industry in general, and the aerospace industry in particular, as a replacement for electrolytic hard chrome plating (EHC). For the majority of aerospace items HVOF is expected to be cost effective and to perform well. Airlines such as Lufthansa, United, and Delta are flight testing HVOF-coated components, and are beginning to adopt HVOF for O&R of landing gear and other items. Manufacturers, such as Boeing Commercial, have used various kinds of HVOF coatings for problem solving on quite a number of components.

HVOF is ideal for line-of-sight applications, including the outer diameters (ODs) of long tubes such as hydraulic and landing gear pistons. It can also be used for shallow internal diameters (IDs) - of depth approximately equal to the diameter - where the flame can be angled into the ID at 45° or more to the surface (and in some cases it is possible to coat deeper by angling as close as 20° to the surface). This means that there are some chrome plating applications that do not lend themselves to HVOF. These include not only IDs of long tubes, such as hydraulic outer cylinders, but also OD coating on small or thin-walled items (especially those made of low temperature alloys such as aluminum) that tend to overheat (above the tempering temperature). The consequences of overheating tend to be loss of tensile or fatigue strength, which is very serious for critical items such as landing gear.

Items not amenable to HVOF coating presently account for about 20% to 30% of DoD depot maintenance work volume, and a replacement process must be found if the Joint Strike Fighter (JSF) is to be chrome-free. Even ID chrome can itself be a problem - thin dense chrome deposition is a difficult process, prone to failure, that can be done by only a few suppliers.

For the DoD depots, HVOF is being demonstrated and validated by the Hard Chrome Alternatives Team (HCAT). The HCAT includes GE Aircraft Engines, Boeing, NAVAIR, and O&R depots from all three services, including NADEPs-Jacksonville, Cherry Point, and North Island, Ogden and Oklahoma City ALCs, NTS-McClellan AFB, and Corpus Christi Army Depot. All three Canadian landing gear manufacturers - Menasco, Messier-Dowty, and Heroux - are teaming with various laboratories and vendors in a Canadian HCAT (C-HCAT), which is being funded by Technology Partnerships Canada (TRP) and the Canadian Department of National Defence (DND). The Program Lead for the HCAT is Bruce Sartwell of the Naval Research Lab, while the C-HCAT is a joint effort with leads at each of the major contractors. The HCAT Technical Lead is Keith Legg, who is also designated to be the technical coordinator and data custodian for the C-HCAT.

The purpose of this program has been to evaluate commercial and pre-commercial chrome alternative technologies and identify those that show the greatest promise for those applications where HVOF cannot be used - primarily IDs, and secondarily heat-sensitive components. Each technology is covered in a Technology Summary in a manner designed to make it possible to compare them directly. At the beginning of this report we identify the types of components that are presently not amenable to HVOF and summarize the criteria we have used to assess the alternatives.

## 2. Current usage of ID hard chrome

### 2.1. Typical ID Coated Components

#### 2.1.1. Introduction

Since the JSF has not yet been designed, we do not know exactly what will be the geometry and materials in the final aircraft. However, by looking at what is currently in general use for military aircraft, we have identified a fairly broad range of different types of items that are frequently chrome plated, but that are not easily amenable to HVOF. In addition, engineers at Boeing and Messier-Dowty have identified specific items on existing systems that cannot be readily HVOF coated.

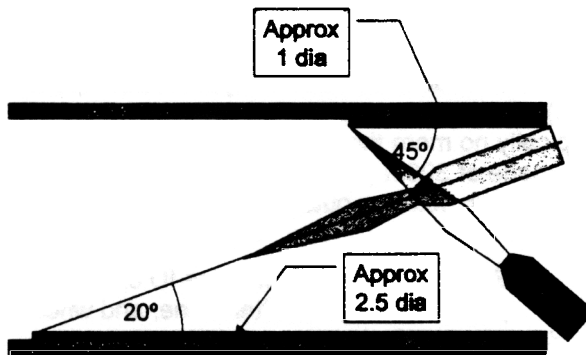
#### 2.1.2. General items

The following geometries are generally problematic for HVOF:

- Holes (blind and through) in hydraulics, including landing gear and actuators
- Pins such as those used in landing gear and actuators
- Lugs and other items where the coating is external, but access to the area is difficult

##### 2.1.2.1. Blind and through holes in hydraulic cylinders

Shallow holes or shallow areas within deep holes can be coated with standard HVOF methods.

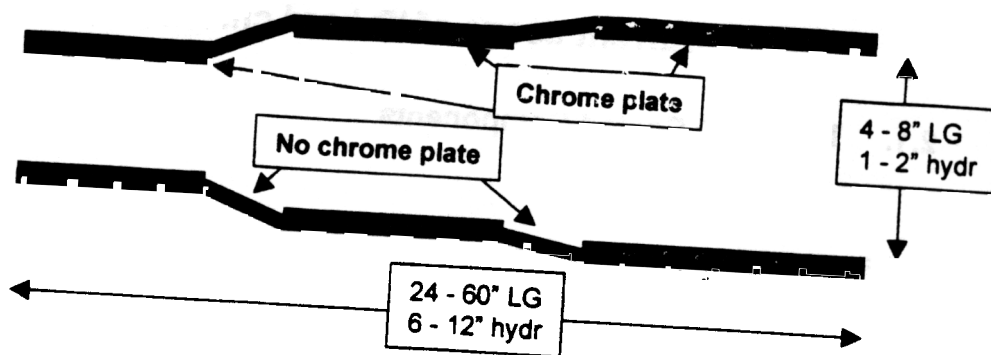


**Figure 1. Small ID coating by HVOF.**

to plate and there are very few vendors capable of doing it.

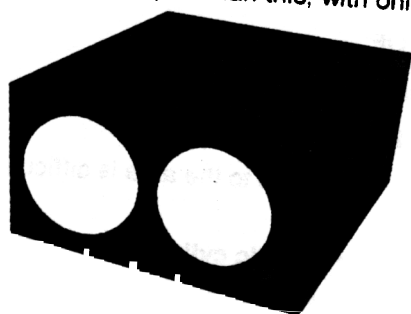
Only on the largest aircraft are the landing gear cylinders large enough in diameter to accommodate a standard HVOF ID gun, which can coat inside holes only above about 11" ID. Outer cylinder IDs of both landing gear and actuators are often chrome plated for wear resistance (against seals) and for corrosion resistance against water contamination in the fluid. In many cases the coating material used is thin dense chrome rather than standard chrome plate. Unlike standard chrome plate, thin dense chrome is quite difficult





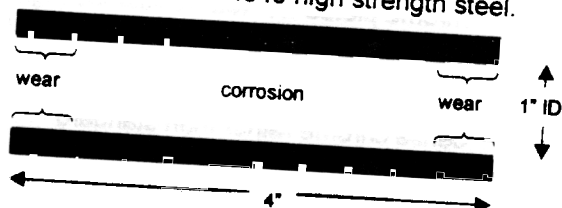
**Figure 2. Complex landing gear outer cylinder cross-section schematic.**

Figure 2 shows a cross section that is quite common in landing gear outer cylinders (although many are simpler than this, with only a single ID). In this case the coating is used only on the working surfaces, and is specified as uncoated on transition areas. When chrome plating cylinders of this type, Heroux uses conformal anodes with insulators to shield the areas where coating is not required. This avoids the complications and waste streams involved in masking difficult areas within the ID. Any replacement coating must either work without shields or it must be able to be shielded easily. Alternatively (and with more difficulty for existing parts) it may be possible to specify that the coating be permitted on the non-working surfaces.



**Figure 3. Hydraulic actuator block schematic.**

Most of these items are basically cylindrical, although hydraulic actuators are often set into a block that contains many different actuators and other hydraulic components (Figure 3). Landing gear typically are several feet long and have large IDs, whereas hydraulics are typically no more than 12 inches long with an inch or so ID. Landing gear outer cylinders are usually made of 300M (or, for the Navy, AerMet 100) high strength steel or 7075 aluminum alloys. Hydraulic actuator outer cylinders are typically 7075 aluminum or 4340 high strength steel.



**Figure 4. Landing gear pin - ID chromed.**

Some landing gear pins are ID chrome plated. This is not often done, and when it is, it is usually to solve a problem such as internal corrosion or fretting and wear at the ends from retainers that fit into the ID. In most cases, however, these items are grease packed to prevent corrosion and end caps are locked in place to prevent wear. In this case, the main demand on the coating is at the ends of the ID, where a protective coating can be deposited with standard thermal spray guns. The ID may be able to be treated by other methods for corrosion. These items represent the smallest IDs we have identified, and because these types of items are seldom ID chromed, we do not expect this to be a problem for the JSF, with proper design.

#### 2.1.2.2. Other difficult geometries

Not all exterior surfaces will be easy to reach with an HVOF gun. Some items have areas that can be readily chrome plated but that will be difficult to access with typical HVOF equipment

For example, lugs on landing gear outer cylinders are frequently chrome plated on the outer flat face to resist wear by retaining caps (Figure 5). In most cases these lugs are positioned so that they can be reached fairly easily and coated with a robotic gun. In some cases, however, the face to be coated is either angled toward the cylinder, making it difficult to reach, or is close to other lugs or parts of the component. In either case, the geometry is complicated and the space in which we can work is limited to about an inch. In most cases, dual lugs are chromed only on the outside, but occasionally we have seen lugs chromed in more difficult areas, where the surface to be coated is partially obscured, as it is in the right hand side of Figure 5.

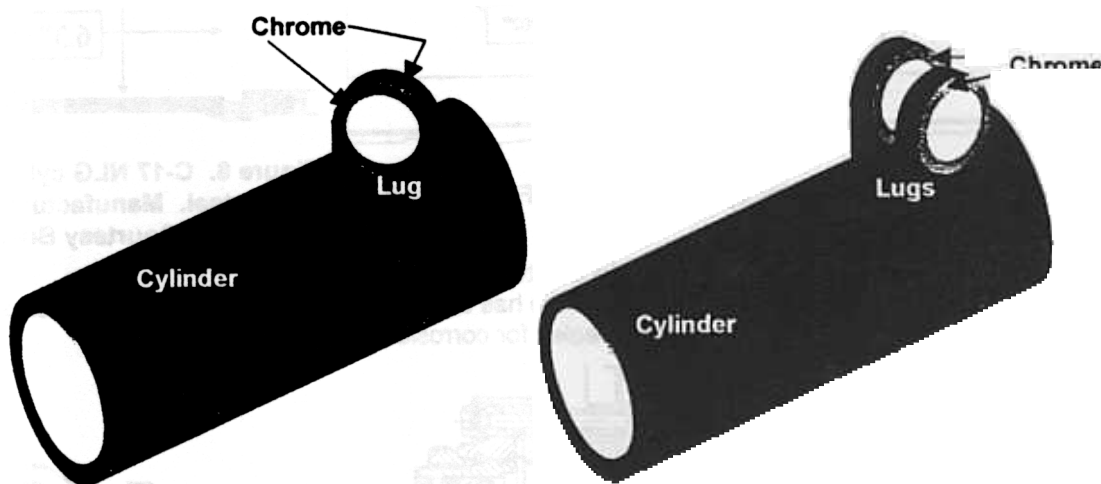


Figure 5. Schematic of landing gear lugs.

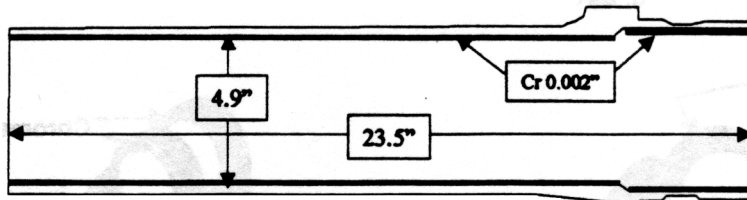
#### 2.1.3. Specific components from Messier-Dowty and Boeing

Internal chrome plating is most prevalent on landing gear components and hydraulic actuators. A number of different types of these components have been identified with Messier-Dowty and Boeing as posing various problems for standard HVOF coating, either because they require ID coating or because access to the area to be coated is difficult. This is by no means an exhaustive catalog of components, but is meant to illustrate the major categories of problems that might be encountered.

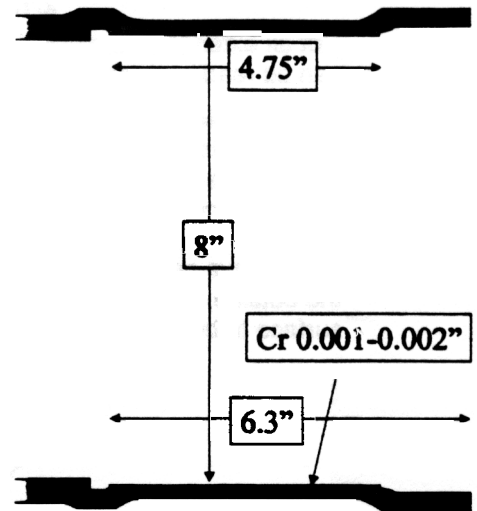
### 2.1.3.1. Actuators and Landing gear cylinders

A much larger landing gear outer cylinder (for the C-17) is shown in Figure 6. In this case, not only is the ID large, but the chrome is required close to the open end, making it fairly easy to HVOF spray at an angle from the open end. The spray angle is 50° to the axis, making a high quality coating possible.

A typical fighter main landing gear outer cylinder is shown in Figure 7. This 4.9" ID item has only one open end and must be coated over a depth of about 2 feet. Note also that the coating is specified to break at the internal ID step, which is quite common with this type of item and requires proper masking.

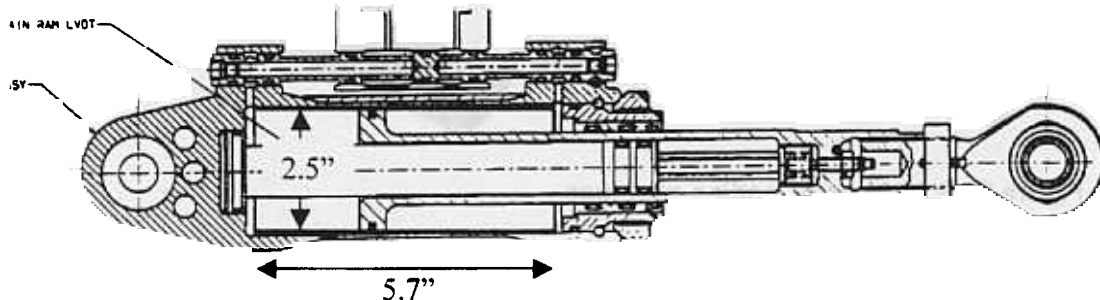


**Figure 7. F-15E MLG outer cylinder bore. B.F. Goodrich, 300M steel. Courtesy Boeing.**



**Figure 6. C-17 NLG cylinder bore, 300M steel. Manufactured by B.F. Goodrich. Courtesy Boeing.**

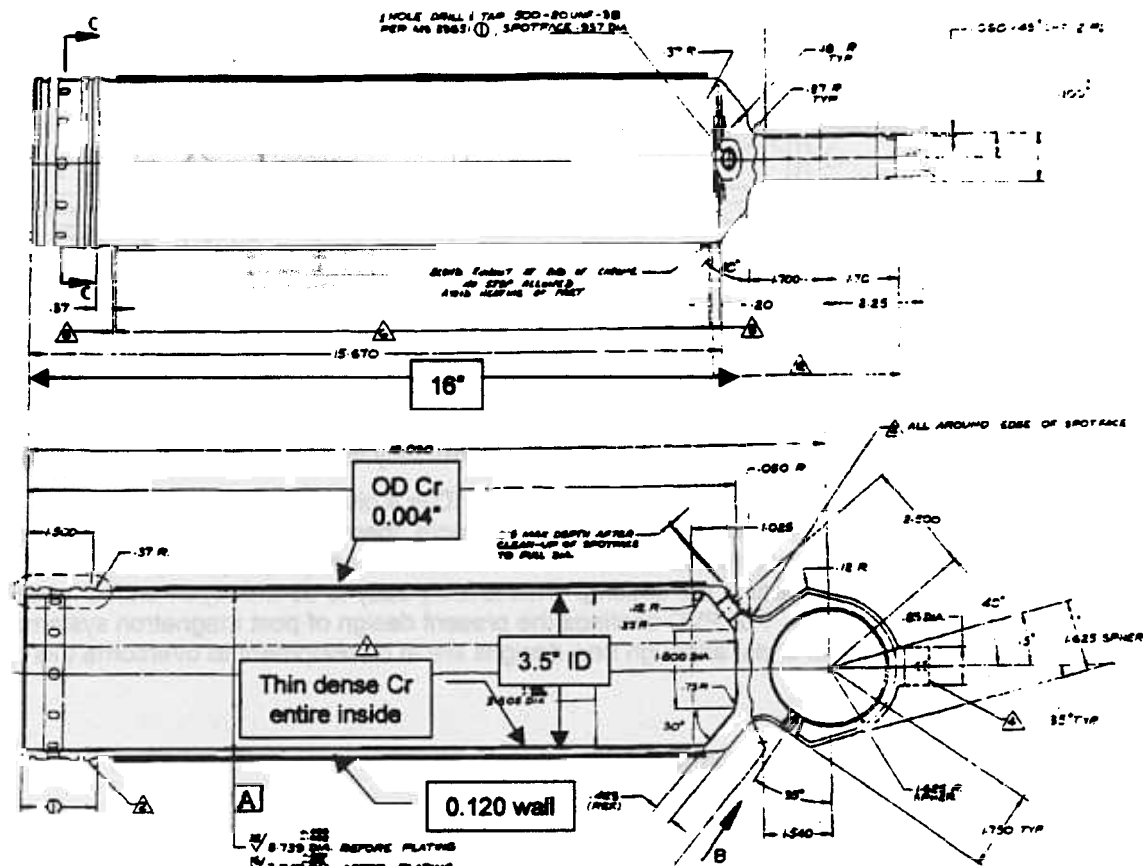
Figure 8 shows a rather typical flight surface actuator - the aileron actuator from an F-18. The 2.5" ID bore has a total depth of about 7" and is accessible only from one end. The chrome is resin sealed for corrosion resistance.



**Figure 8. F/A-18 E/F aileron servocylinder, manufactured by HR Textron - Courtesy Boeing.**

Flight surface actuators are frequently smaller in diameter than that of Figure 8 - with some smaller actuators having IDs of about 1".

Landing gear and landing gear actuators built by Messier-Dowty frequently call out standard hard chrome (0.005" thick plate) on the OD and thin dense chrome (0.0005 - 0.0008" thick on the ID).

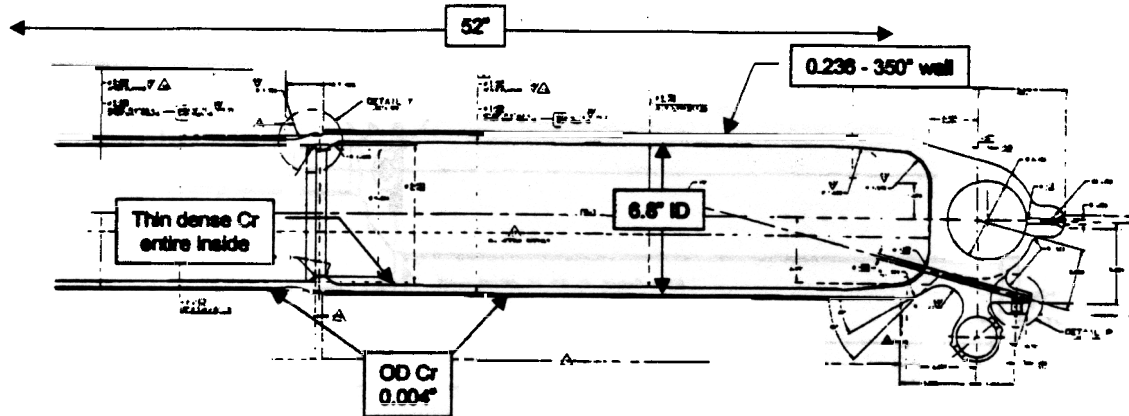


**Figure 9. Landing gear actuator inner cylinder, (300M high strength steel). Courtesy Messier-Dowty.**

The inner cylinder of a high strength steel actuator of this type is shown in Figure 9. The OD chrome plate can be readily replaced by HVOF coatings. Its purpose is to provide a wear resistant surface to bear against the guide bushing and to prevent wear of the outer cylinder seals. The thin dense chrome on the inside is for a combination of corrosion resistance and wear resistance against internal seals.

The ID chrome cannot be replaced by HVOF WC-Co using current HVOF equipment. It could be replaced by plasma sprayed WC-Co, since the ID will accommodate a standard plasma spray ID gun. However, in order to make the internal coating a drop-in replacement, the coating would have to be less than 0.001" thick, with low enough porosity to prevent corrosion or leak-by, and the gun would need to coat both the walls and the end. Since the wall thickness is only 0.12", heat from the gun would have to be dissipated effectively, which could presumably be done by cooling both the inside and the outside of the cylinder.

A larger landing gear actuator inner cylinder is shown in Figure 10. It is very similar to that of Figure 9, but is about twice the size. Any method used to coat this item internally would require a reach of about 6 feet, and would need to coat approximately 1,100 square inches uniformly and cost-effectively. Again, the OD chrome is readily replaced by HVOF WC-Co.



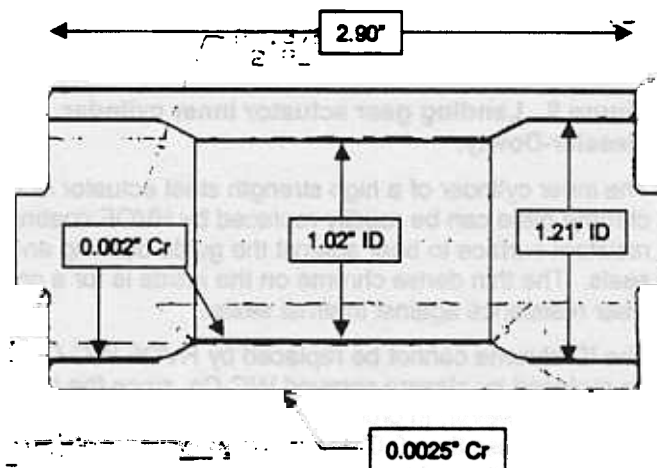
**Figure 10. Landing gear actuator inner cylinder - courtesy Messier-Dowty (300M steel).**

We should also note that in both of these actuators the ID is a blind hole. Some coating methods have more difficulty with blind holes - for example, thermal sprays must have overspray powder (i.e. powder that is not melted and bounces back off the part) rapidly swept out of the area to avoid their entrainment in the coating. This is fairly easy to do with open-ended tubes, but difficult with blind holes. For PVD coatings the present design of post magnetron systems requires access from both ends, although new designs are in development to overcome this limitation.

#### 2.1.3.2. Landing Gear Pins

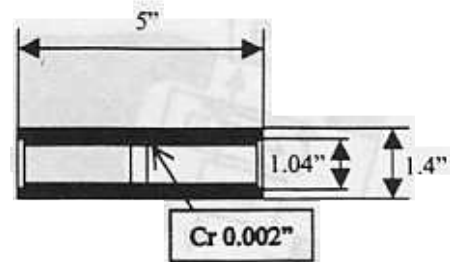
In contrast to these large items, landing gear pins are some of the smallest landing gear components that are frequently chrome plated. In most cases pins are chromed only on the outside to resist wear and galling. In some cases, however, the IDs of pins must be coated to protect them from wear against locking devices and end caps, and to provide additional corrosion protection. Figure 11 shows such an internally chromed pin. This is the smallest diameter that we have found for landing gear components.

The 1.21" diameter recesses on the ends of such a pin could be readily coated by an HVOF gun angled into the ID. The 1.02" ID is more difficult to HVOF spray. However, the area could be reached with a torch angled at 30° to the axis of the pin. While this is far from an ideal impingement angle and does reduce the quality of the coating (increased porosity and reduced adhesion), coating quality is frequently adequate under these conditions, since high wear is not an issue. If needed for corrosion prevention, the deepest HVOF coating could be polymer-sealed, which is often done with chrome plating. Therefore we believe that this component could be HVOF coated inside and out.



**Figure 11. 300M pin for MLG shock strut piston - courtesy Messier-Dowty.**

In contrast to the pin shown in Figure 11, the F/A-18 nose landing gear torque arm pin shown in Figure 12 is the same diameter, but longer, and is unlikely to be ID coated reliably with current HVOF equipment, since the spray angle required to reach the center would be about 20° to the axis. GEAE reports that in some cases HVOF spray can be done at this angle, but the reliability of such a coating within the narrow confines of this component would be suspect.

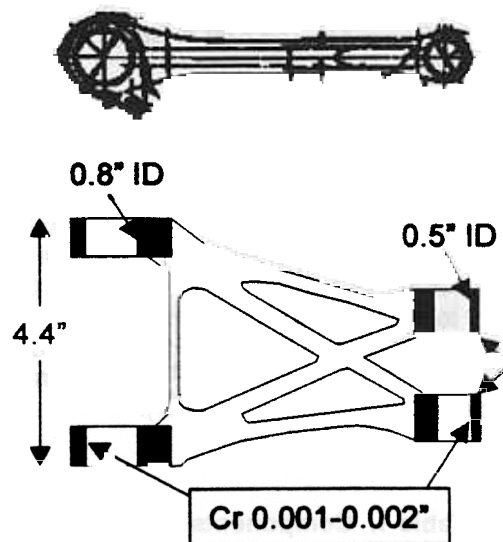


**Figure 12. F/A-18 E/F NLG torque arm pin, Aermet 100. Manufactured by Messier-Dowty. Courtesy Boeing.**

### 2.1.3.3. Other components

Most other components do not have deep IDs such as those found in actuators and landing gear. However, some do have small IDs, areas that are difficult to reach, or areas where heat dissipation could be a problem. In most cases these components do not pose serious problems for HVOF coating, but in some, standard HVOF equipment is not capable of coating them easily or reliably.

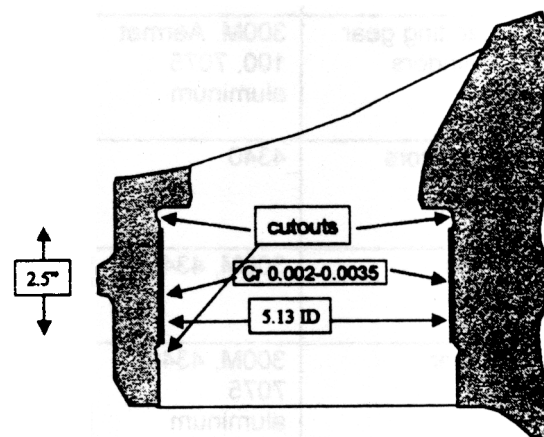
Figure 13 is an example of an item that, while not trivial to HVOF spray, could be coated with existing equipment. The four lug holes, which require 0.002" of chrome plate, can be coated by rotating the component in front of the flame, although care must be taken to prevent overheating. Some landing gear components of this general shape, however, require chrome plate on the faces of the lugs, as shown by the arrows on the right of the figure. In these cases, access is quite difficult, and standard HVOF equipment would not be able to reach these areas easily.



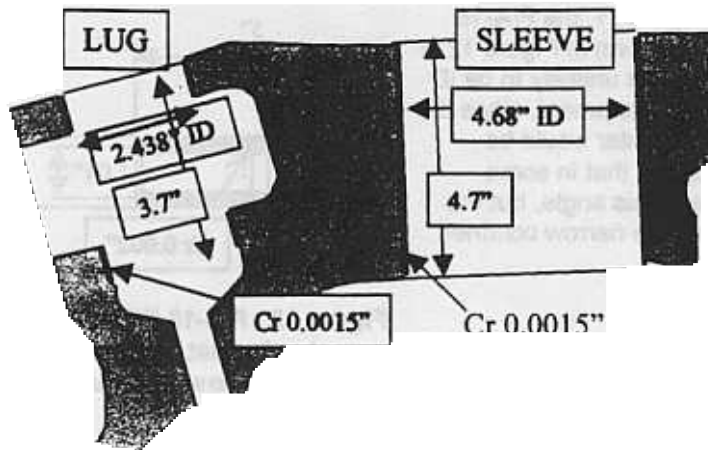
**Figure 13. F-15 Torque arm lugs. 300M steel, Menasco/Goodrich. Courtesy Boeing.**

Another lug is shown in Figure 15, page 10. In this case, HVOF coating of the sleeve ID would be relatively simple. However, ID coating of the lug hole would be much more difficult because of the depth of the hole and the fact that it is almost closed on one end. Plasma spray coating of this part would be possible, since the diameter exceeds 3".

A different type of situation is illustrated in Figure 14. The area is readily accessible from below provided the rest of the part does not interfere with the gun. Access from above would be restricted by the ID "overhang", which shields the top of the ID coating area. This type of component could be satisfactorily thermal spray coated using an ID plasma spray gun brought in from above.



**Figure 14. C-17 MLG swivel pin.**



This item illustrates a further consideration in ID coating. Note that there are cutouts which are required to be free of coating, and must, therefore, be shielded to prevent their being sprayed. While this shielding is somewhat easier than that typically used for chrome plating, its design and fabrication (typically of thin steel sheet) is something that needs to be considered in designing a part for ID spray coating.

**Figure 15. C-17 MLG brace lugs. 300M, Goodrich  
Courtesy Boeing.**

#### 2.1.4. Summary of component coating requirements

The primary parameters of the different types of components are summarized in Table 1, together with applicability of non-HVOF thermal sprays. The fact that HVOF can only be used for components above 11" ID restricts the current HVOF method to only the largest landing gear, or to shallow IDs whose depth is no greater than about one diameter. Plasma spray could be used for almost all landing gear outer cylinder IDs, but is currently too porous. This problem might well be solvable by the use of small- or nano-particle spray methods (which should also permit coatings to be thinner).

**Table 1. Components and most widely applicable thermal spray coating technologies.**

| Component              | Typical materials               | Typical size range          | HVOF shortfall                         | Other thermal spray methods |                        |
|------------------------|---------------------------------|-----------------------------|--|-----------------------------|------------------------|
|                        |                                 |                             |  | Plasma spray                | Nano spray             |
| Landing gear cylinders | 300M, Aermet 100, 7075 aluminum | 5"-12" ID<br>24" - 60" long | Diameter too small, depth too large    | Too porous                  | ✓?<br>May be too large |
| Actuators              | 4340                            | 1"-3" ID<br>6"-12" long     | Diameter too small, depth too large    | ✓                           | ✓                      |
| Pins                   | 300M, 4340                      | 1"-2" ID<br>3"-6" long      | Diameter too small                     | Too small                   | ✓                      |
| Other                  | 300M, 4340, 7075 aluminum       | Variable                    | Partially hidden lugs, thin walls, etc | ✓                           | ✓                      |

Some other general observations on coating requirements are also of importance:

- While OEM coating thicknesses are indicated in the figures above, depot rebuild may require thicker coatings - up to 0.010" in final thickness (0.020" pre-ground thickness). Therefore, coating technologies must span a wider range (0.0003" - 0.020") than is typical with OD coatings.
- Extreme wear and corrosion resistance are usually not required for ID coatings - i.e. their mechanical and chemical properties are not generally as stringent as for ODs.
- Very high density (low porosity) coatings are required for landing gear cylinder IDs to prevent gas leakage at their high operating pressures. This precludes standard plasma sprays.



## **PART B - SUMMARY OF REPLACEMENT CRITERIA AND OPTIONS**

In this section we summarize the differences between OEM and O&R use, the criteria that a viable ID chrome replacement must meet, and our findings on which options are the most viable or the most easily brought to production for ID chrome replacement.

### 3. OEM and O&R requirements

The requirements for OEM and O&R chrome replacement are somewhat different. One of the primary differences, although difficult to quantify, is that at the OEM the processing environment is quite well defined, whereas in O&R operations many different components must be processed, each with its own unique problems. Some of the major differences are summarized in Table 2.

**Table 2. Some differences between OEM and O&R chrome replacement.**

| OEM  | O&R  |
|--|--|
| Limited numbers of different components, processed in significant quantities on a regular basis. Standard production lines | Many different components, sporadic work loads   |
| New substrate material; only new coatings need be stripped in case of processing errors                                    | Old, dirty substrates; old coating must be stripped prior to recoat. Coating must withstand component cleaning and servicing |
| Coating thickness typically 0.0003" (thin dense chrome) to 0.004"  | Coating thickness up to 0.020" as-coated, 0.010" finished, for rebuild   |
| Approvals from OEM engineers   | Approvals from OEMs, NAVAIR, ATCOM, Single Item Managers, Program Managers   |

One issue to consider very carefully is whether a process for OEM can also be used for O&R. Although in principle there is no reason that O&R processes cannot be different from OEM processes, it makes validation and acceptance doubly expensive and time-consuming if two different processes must be validated, rather than a single one accepted by OEMs, DoD stakeholders, and depots alike. This is an especially important issue in view of the wide range of coating requirements for ID chrome replacement, from 0.0003" to 0.015" thick. Some processes are good for OEM use but cannot be used for rebuild, while others cannot reliably deposit a coating thinner than about 0.001".

### 4. Hard chrome replacement criteria

The following is drawn from the Brooks AFB Statement of Need describing the basic requirements for a chrome replacement<sup>1</sup>:

*"A coating process (or processes) is needed that will meet the requirements of chromium without the environmental and health hazards associated with chromic acid. Ideally, the process would not use any EPA 17 chemicals. The process must not cause hydrogen embrittlement. Fatigue loss should be no worse than electro-deposited chromium. The deposit should exhibit adhesion to steel equivalent to electro-deposited chromium. The deposit must be machinable or grindable to produce surface finishes of approximately 8 rms. The deposit must be easily strippable. Good corrosion protection would be a plus. The finished surface must have low friction characteristics and must not gall. The process should be relatively easy to control. It should not require large amounts of capital to install and should fit into existing space."*

Replacing hard chrome involves a great deal more than meeting the technical requirements for wear, corrosion, fatigue, etc. To be viable in the aerospace community the replacement must fit into the way the industry works at both the OEM and O&R level (commercial shops and military

<sup>1</sup> "USAF FY96/97 Environment, Safety & Occupational Health Research, Development & Acquisition Strategic Plan", Published by the Human Systems Center, Brooks AFB (1996).

depots). Technical performance cannot be considered in isolation from other technical issues such as stripping and finishing, from environmental and safety issues, from issues of complexity and cost, or from the more “political” issues of acceptance and validation. The most important criteria that an alternative must meet to replace chrome successfully on IDs are summarized in Table 3, page 16. There are many more detailed issues, but these will in general be different for each different application.

The HCAT team started out with the approach that, to be viable, a hard chrome alternative must meet the same performance standards as hard chrome in all critical areas (as we have indicated in Table 3). As a practical matter, however, the team has found that the alternative must **exceed** the performance of hard chrome. If it does not, there is no strong driver to specify the replacement, since all changes of this type involve both cost and risk. In general, environmental drivers are very weak, especially in an industry as complex as aerospace, where responsibility for change is diffused and decision makers are often not directly affected by their decisions. However an alternative will be strongly and rapidly embraced by engineers and other stakeholders if the replacement provides a clear technical and cost benefit, and especially if it provides some critical capability that chrome lacks.

## 5. Summary of options

The options for chrome replacement are summarized in Table 4, page 17. The assessment of each technology is based on how well it meets the criteria of Section 4 and on what it would take to bring it to production on IDs and heat-sensitive components. Our overall assessments are as follows:

**For immediate use** - The only immediately viable option is electroless nickel. Electroless nickel composites are also good technical options but will need development and validation, and may not be suitable for O&R. However, because Ni is on the EPA-17 list we do not recommend this approach except if needed for the short term.

**Short term development** - For the short term (2 years) there are several options:

- In electroplating technology, the cobalt-based composites (of which the only one we have found to be in production is Praxair's Tribomet®) are an option that avoids the use of EPA-17 materials. This method is already in production for some components, but there are unknowns for chrome replacement, such as whether it would require heat treating. However, Boeing's experience with composites indicates severe potential problems when using composites in production, especially for periodic (O&R), rather than continuous (OEM) use.
- Plasma spray can already be done in IDs > 3" with ease, and > 1.5" with more difficulty, which would solve most of the requirements for hydraulics. However, it would not solve the needs of landing gear main cylinders, which require less porous coatings. The advantage of this approach is that it can be used to deposit the same materials as are being deposited on ODs by HVOF, namely WC-Co and WC-CoCr.
- Electrospark microarc welding looks promising, with some caveats concerning fatigue due to the heat-affected zone and cracking of coatings due to repeated thermal cycling during deposition. The method can only be used for small IDs, and can deposit WC-Co and Cr<sub>3</sub>C<sub>2</sub>-Co, so that it could be used in tandem with plasma spray.

**Intermediate term development** - For the intermediate term (OEM production in 2 years, O&R in about 5 years) there are two main options:

- Small- or nano-particle plasma spray looks very promising to overcome the problems inherent in standard plasma spray, making coatings denser, smoother, and suitable for use in landing gear, and reducing component heating.

- Post magnetron PVD of metals and alloys may be an option if the materials perform satisfactorily and if the equipment can be properly integrated into the IVD systems currently in use at OEMs and depots.

**Long term development** - Chemical vapor deposition (CVD) is one of the best means of depositing thick coatings on even the smallest IDs, but it is generally entirely unsuitable for most structural components because of high deposition temperature and worker safety. However, over the long term (OEM production in 5 years, O&R in about 8 years) there are two possible CVD methods that might become viable:

- Combustion CVD is a particularly simple approach, but is rather limited in materials that can be deposited (primarily oxides). Not enough is known about it at present, but it would have low capital cost and is quite flexible.
- Plasma CVD is now being done over large areas for ODs and complex shapes. It could be adapted to IDs, where it might be possible to deposit materials that would be both hard enough and thick enough for chrome replacement. This is likely to be a relatively high capital cost approach.

**The details of all the technologies we have evaluated are given in Part C.**

**Table 3. Hard chrome replacement criteria.**

| Issue                            | Criteria  | Notes  |
|----------------------------------|---|--|
| <b>ID coating requirements</b>   |   |  |
| Hole dimensions                  | Actuators: 1" min. dia. by up to 24" long<br>Landing gear, large actuators: 3-15" dia by up to 60" long |  |
| Hole geometry                    | Open, blind, some internal grooves  |  |
| Coating thickness                | OEM: 0.003"<br>OEM thin dense Cr: 0.0003"<br>O&R: 0.003-0.015"  |  |
| Smoothness                       | 16 $\mu$ " Ra typical, some replacements may need to be 4 $\mu$ " Ra                                    | Highly useful to be able to be able to deposit thin coatings to replace thin dense Cr, without need for grinding. (As-deposited Ra<8 $\mu$ ".) |
| Deposition temperature           | High strength steels: <250C<br>Aluminum alloys: <150C   | Critical issue is time-at-temperature. Critical issue is fatigue reduction due to changed surface microstructure.                              |
| <b>Technical issues</b>          |   |  |
| Wear resistance and hardness     | Match performance of chrome on actual components  | Critical issue is wear life (wear rate x thickness) in service, and avoidance of seal wear in hydraulics                                       |
| Corrosion resistance             | Must match chrome - primarily B117 salt fog   | Microcracks make chrome a poor corrosion inhibitor - may require sealer or Ni underlay.  |
| Hydrogen embrittlement           | None  | This is a critical flight safety issue   |
| Fatigue                          | Fatigue debit must not exceed chrome  | Navy particularly concerned with NaCl and SO <sub>2</sub> atmospheres - critical flight safety issue.  |
| <b>Producibility</b>             |   |  |
| Reproducibility                  | Process must be stable  | Both OEM and O&R environments  |
| Process window                   | Within day-to-day operating parameters  | Simple, reasonable QC needed   |
| Cost                             | Total production cost comparable to 2 x chrome.<br>Life-cycle cost < chrome<br>Reasonable capital cost  | Production cost needs to include cleaning, masking, finishing, heat treating, waste disposal, etc.   |
| <b>OEM and O&amp;R fit</b>       |   |  |
| Stripping                        | Must be able to be stripped - safe chemicals, water jet, etc  | Strippability is <u>crucial</u> to O&R.  |
| Field and O&R chemical stability | Must withstand O&R cleaning, chemicals, hydraulic fluid, etc.   | Must not deteriorate when put through O&R process  |
| Environment/safety               | Must be environmentally benign and safe for workers   | Note that O&R operations are more diverse and less easily controlled   |
| <b>Acceptance issues</b>         |   |  |
| Specifications                   | AMS and/or aircraft company specifications needed   | Cannot be specified and put on drawings without specs.   |
| Proprietary technology           | Cannot be proprietary to one company  | If possible, should be able to be done at general O&R site to avoid sending out  |

**Table 4. Summary of ID chrome replacement options.**

| Technology                             | Principle                            | Company   | Capabilities/Notes   | Status OD            | Status ID         |
|--|--------------------------------------|---|--|----------------------|-------------------|
| <b>Thermal spray</b>                   |                                      |   |  |                      |                   |
| HVOF                                   | Powder + high temperature flame      | e.g. Sulzer Metco, Praxair, TAFA                      | 11" ID, WC-Co, alloys  | Production           |                   |
| Plasma spray                           | Powder + plasma                      | e.g. Sulzer Metco, Praxair                            | 1.5" ID, WC-Co, alloys, metals                                   | Production           | Production/short  |
| <b>Weid coating</b>                    |                                      |   |  |                      |                   |
| Electrospark (ESD)                     | Microarc weld                        | Advanced Surfaces and Processes, Battelle PNL         | <0.5" ID, 120" long nanophase WC-Co, alloys. Small diameter only | Development          | Development/short |
| Explosive clad                         | Explosive bonding                    | SigmaBond Technologies                                | Metals, WC-Co  | Research             |                   |
| <b>PVD/CVD</b>                         |                                      |   |  |                      |                   |
| CVD, MOCVD, plasma CVD                 | Deposition from gas                  | Various   | Very small, long holes. High temperature/dangerous precursors    | Production           |                   |
| Combustion CVD                         | Precursors combined in flame         | MicroCoating Corp                                     | Compounds (oxides, etc.) VOC solvents used                       | Research Development | Research/long     |
| Plasma CVD                             | Precursors deposited by plasma       | Metroline   | Oxides, nitrides, metals   | Production           | Research long     |
| Hollow cathode evaporation             | Small internal hollow cathode        | U. Uppsala (Sweden)                                   | Metals, nitrides. Low build-up                                   | Research             |                   |
| Laser deposition                       | Laser evaporation, alloying, and CVD | QQC Diamond   | Diamond. No build-up   | Research             |                   |
| Laser Induced Surf. Improvement (LISI) | Laser alloying                       | Surface Treatment Technology, University of Tennessee | Alloys with surface material (not coating). No build-up          | Research             |                   |
| Plasma nitride                         | Nitriding at about 500C              | e.g. Advanced Heat Treat                              | Surface treatment (no build-up, high temperature)                | Production           |                   |
| <b>Wet plating</b>                     |                                      |   |  |                      |                   |
| Brush plating                          | Ni electroplate                      | Various   | Cr, Ni, other metals   | Production           |                   |
| Alloy plating                          | Electroplating of simple alloys      | Various   | Ni-W-B, Co-W   | Production           | Production/short  |
| Co-composites, Tribomet®               | Co alloy composite plate             | Praxair   | Co alloy, proprietary  | Production           | Production/short  |
|  | Short term (/short)                  |   | Long term possibilities (/long)                                  |                      |                   |

## **PART C - PROCESS SUMMARIES**

In the following subsections we present detailed Process Summaries for the processes we have considered, which include descriptions of processes and evaluation of how they fit with the criteria for OEM and O&R chrome replacement. Different levels of detail are incorporated depending on the viability of each method for ID chrome replacement. For the most promising methods we have included significantly more detail on cost issues and technical performance than for those technologies that are not viable replacements.

## 6 Process Summary Thermal Spray



## 6.1. Introduction

Thermal sprays are standard hard coating and repair methods for aerospace components that are now in widespread use at OEMs, commercial O&R shops, and DoD depots. Their primary aerospace uses are

- turbine engines (shafts, turbine blades, thermal barrier coatings, erosion coatings, abradable coatings, anti-fretting coatings)
- landing gear, flap and slat tracks, and for spot problem-solving in high wear areas
- chrome replacement for landing gear inner cylinders, axles and pins

**Table 5. Summary information - Thermal Spray**

|                              |  |
|------------------------------|--|
| <b>Process name</b>          | Thermal spray (plasma spray, HVOF)   |
| <b>Description</b>           | Powder fired through flame or plasma softens and builds up coating   |
| <b>Coating materials</b>     | WC-Co, Cr <sub>3</sub> C <sub>2</sub> -NiCr, oxides (e.g. Al <sub>2</sub> O <sub>3</sub> , Cr <sub>2</sub> O <sub>3</sub> ), alloys (e.g. Stellite, Tribaloy)  |
| <b>Temperature</b>           | 150 - 400C surface temperature of part during deposition   |
| <b>Minimum ID</b>            | 1.5" (plasma spray), 11" (HVOF)  |
| <b>Maximum depth</b>         | 26" standard. Can go to almost any depth   |
| <b>Stage of development</b>  | Production   |
| <b>Primary advantages</b>    | Direct fit with existing thermal spray chrome replacements (methods and materials).<br>Capable of OEM and rebuild use.<br>Direct fit with current O&R methods. |
| <b>Primary disadvantages</b> | Plasma spray not as dense as HVOF.<br>Difficulties with coating quality in blind holes.<br>Heat removal in confined spaces.                                    |

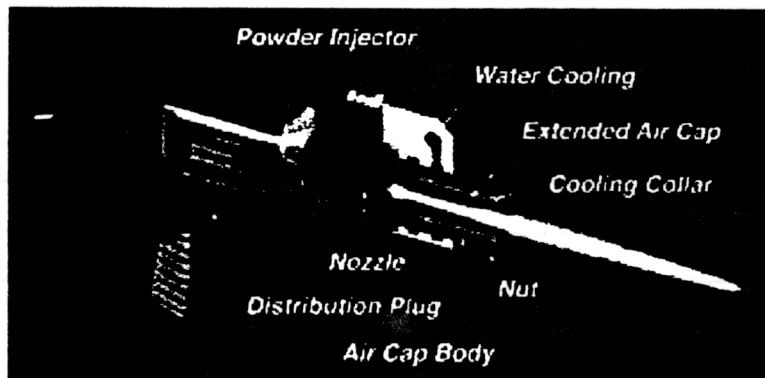
## 6.2. Process description

The basic thermal spray process consists of firing a powder comprising particles in the typical size range of 20-60 microns (entrained in a high-velocity carrier gas stream) through a source of heat. The heat softens the powder particles, which hit the substrate at high speed and flatten in pancake-shaped "splats". As they overlay each other these splats form a continuous coating, often merging the boundaries of the individual splats into a coherent coating material. The method can be used for spraying alloys, ceramics, or cermets such as WC-Co. In the latter case, only the matrix Co softens, leaving the WC particles embedded in the coating. The two highest quality thermal spray methods, which are the only two relevant to our purposes, are HVOF and plasma spray.

### 6.2.1. High Velocity Oxy-Fuel (HVOF)

HVOF coatings are the highest quality thermal spray coatings. The principle of HVOF coating is to use a supersonic flame, which raises the particles to high (although usually sub-sonic) velocity. When they hit the substrate these high-velocity particles form a very coherent, low porosity coating. There are two basic forms of HVOF equipment -

1. Continuous flame HVOF (equipment made by companies such as TAFE and Sulzer-Metco). Continuous flame equipment is the only commercially available HVOF equipment. In the standard commercial HVOF gun, oxygen and fuel (usually hydrogen, acetylene, or kerosene) are mixed and burned in a combustion chamber, forming a stream of hot gas that comes out of the end of the gun. Powder is injected axially into the flame, where it heats and softens on its way to the substrate surface. The stand-off (gun to substrate distance) must be sufficient to heat the particles adequately before they strike the substrate.
2. Detonation Gun (D-Gun) and Super D-Gun (explosive equipment and process proprietary to Praxair). In the D-gun the fuel and oxygen are mixed and ignited by a spark. The consequent explosion projects the powder and hot gas at high velocity onto the substrate.



HVOF can be used to deposit most alloys and cermets such as WC-Co, WC-CoCr,  $\text{Cr}_3\text{C}_2\text{-NiCr}$ , etc. The flame temperature is insufficient for most ceramics, such as oxides.

Because the flame produces a great deal of heat (and the particles themselves are hot) the substrate temperature must be moderated by air-jet cooling using jets set up around the object being coated. The gun is also

**Figure 16. HVOF gun (Sulzer-Metco Diamond-Jet).**

moved over the surface (or the surface under the gun) at a speed sufficient to prevent heat build-up in any area.

The method tends to be very forgiving, with a wide process window (especially with regard to the stand-off, which is important for coating complex parts). Coatings are usually hard, with excellent adhesion and very low porosity (typically >98% density). For this reason they can be machined without chipping to form a smooth, non-porous surface. HVOF coatings are the only thermal sprays with sufficiently low porosity to prevent leak-past in high pressure landing gear cylinders (typically 7,000 psi).

Because the flame is supersonic, the process must in general be done in a sound-proof room typical of other thermal spray processes, but with better acoustic insulation. The coating is normally applied using a standard industrial robot. Overspray (powder that misses or bounces off the substrate) must be caught in a standard bag-house filter system.

The process requires the following steps

1. Gross cleaning (oil, grease, paint, rust removal). Waste stream - cleaning chemicals typical of all parts cleaning and depainting.
2. Grit blasting to roughen the surface and give a strong mechanical lock between substrate and coating. Waste stream - grit, which may be contaminated with metal particles, including chrome alloys.

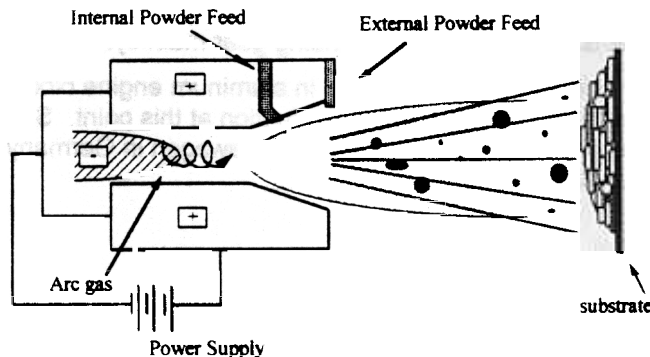
3. Masking - usually mechanical (metal strips)
4. HVOF spraying. Waste stream - overspray powder, CO<sub>2</sub> and H<sub>2</sub>O combustion products.
5. Grinding (usually diamond or borazon wheel). Waste stream - spray material contaminated coolant.
6. Superfinishing, if needed (vibratory stone honing for a very smooth surface). Waste stream - spray material contaminated coolant.

The HVOF process uses very high volumes of process gases - typically hydrogen and oxygen. A full day's spraying would typically use 16 standard tanks of hydrogen (used 8 at a time). In some DoD locations storage of this amount of flammable gas is considered a hazard, and in others HVOF spray rooms are required to be explosion-proofed with special vent systems.

HVOF coatings are currently being used on landing gear and other airframe components by Boeing Commercial and on slat and flap tracks by Messier-Dowty. They are being qualified for use on landing gear by Lufthansa, Delta, and United Airlines. The Hard Chrome Alternatives Team (HCAT) is demonstrating and validating them for O&R chrome replacement on landing gear, propeller hubs, hydraulics, and other aircraft parts serviced in DoD depots, while the Canadian-HCAT is doing the same for landing gear manufactured in Canada.

### 6.2.2. Plasma spray

Plasma spray is more commonly used than HVOF, since it is cheaper and easier to do, and is more versatile in the materials it can deposit. Coating quality is high, but coatings tend to be more porous and not as strongly bonded as HVOF coatings.



**Figure 17. Plasma spray schematic.**

In this case, the heat source is a thermal arc struck between an electrode and the body of the gun. Typically this arc runs at about 60 V and 600 A. Since the temperature in such an arc is very high (thousands of degrees C), it can be used to spray almost any material, including oxide ceramics. Gas and particle velocities are much lower than in HVOF, and consequently the quality of the coating (in terms of adhesion and porosity) is lower. Typical density is 95% of theoretical.

In most plasma spray locations the plasma spray set-up is very similar to that used for HVOF - a spray booth with some acoustic isolation, air ducting and a bag house to trap overspray, robotic application, and air jet cooling.

The plasma spray process and preparation is similar to that used for HVOF, and the waste streams are consequently essentially the same, though plasma spray processes do not produce combustion products. The powder is generally carried on a stream of dry argon or nitrogen, while the arc gas is commonly argon.

### 6.3. State of development

Both HVOF and plasma spray are fully developed commercial processes in widespread industrial and aerospace use. Equipment and powder can be obtained commercially from a number of vendors. There are numerous commercial, military, and aerospace specifications for thermal spray processes, the most recent being AMS 2447 for HVOF coating.

The coating material most commonly used for chrome replacement with both thermal spray and HVOF is WC-Co (usually WC-17Co or WC-12Co). HCAT has chosen WC-17Co because it is easier to spray and less brittle than WC-12Co, while having similar performance. While its wear and fatigue properties are excellent (see below), WC-10Co4Cr has superior corrosion resistance. For this reason C-HCAT and Lufthansa have chosen to use WC-CoCr. Note, however, that the chrome in the coating is not hexavalent, but metallic (as it is in stainless steel), and there is no evidence that it becomes hexavalent on stripping.

At this point, all data on performance, producibility, and cost show that HVOF is at least as good as (and usually better than) hard chrome. Validation and flight testing on both HVOF WC-Co and WC-CoCr to replace hard chrome in OEM and O&R use is under way at Boeing, Lufthansa, Delta, United Airlines, HCAT, and C-HCAT.

### **6.3.1. ID coating**

There are fully qualified and commercially used thermal spray ID coating guns and processes for both HVOF and plasma spray. Equipment for both methods is available commercially from manufacturers such as Sulzer Metco and Praxair.

#### **6.3.1.1. HVOF ID coating**

Standard HVOF guns can be used to coat shallow IDs by angling the gun into the end of the hole. Holes can easily be coated to a depth of about one diameter in this manner, although success has been reported of coating to depths of more than two diameters by angling the gun to within about 20° of the inner surface. In this way it is possible to ID coat a through hole with a depth of 4 or more diameters.

For deeper holes, one must insert the gun into the hole. However, because of the large stand-off and the physical size of the equipment, HVOF is limited to diameters of at least 13" and depths of 24" with the Diamond Jet ID gun. This is too large even for landing gear main cylinders.

GM has developed an HVOF system for spraying the cylinder IDs in aluminum engine blocks with a wear-resistant steel, but the method is not in commercial production at this point. Sulzer-Metco has installed a commercial engine block arc-spraying line for Volkswagen in Germany, which seems to be superceding the GM approach.

#### **6.3.1.2. Plasma spray ID coating**

Plasma spray is currently used for coating IDs in the aircraft industry. GE Aircraft Engines uses a Sulzer Metco gun to coat a small (approximately 1.5" diameter) slot for turbine blades. Praxair is currently replacing chrome plate with plasma sprayed Tribaloy in the IDs of the blade dampers on all the Navy's CH-53 7-bladed heavy-lift helicopters. These dampers are approximately 2.5" ID by 7" long and 3.25" ID by 8" long. Tribaloy is being used because it was already tested. WC-Co has since been optimized for this type of application and it would quite probably have been used had it been ready in time.

Sulzer-Metco makes a number of ID guns for plasma spray coating, as well as a rotary power and gas manipulator called a RotoPlasma 500™. The commercially available equipment is summarized in Table 6.



**Figure 18. CH-53 helicopter.**

**Table 6. ID plasma guns.**

| Gun type   | ID (in) | Depth (in) | Power (kW) | Notes   |
|------------|---------|------------|------------|---|
| SM-F210    | 2.4     | 26         | 12         | Sulzer Metco. Matches to modern Rotoplas unit                               |
| 11MB       | 1.75    | 24         | 25         | Sulzer Metco  |
| SM-F100    | 4       | 22         | 20         | Sulzer Metco  |
| 7-MST      | 1.625*  | 13*        | 24         | Sulzer Metco. Extension to 9MB plasma gun. Used by GEAE for dovetail slots. |
| Micro-mini | 1.5     |            |            | Praxair. Not currently in commercial production.                            |

\* According to Sulzer-Metco engineers, it may be possible to use this gun for 1" ID by 18" deep.

There are a number of caveats with ID thermal spray coating.

1. Sulzer-Metco generally recommends their SM-F210 gun with a RotoPlasma unit for IDs greater than about 3". They generally recommend better materials rather than coatings for smaller IDs, because smaller ID coatings are more difficult to do.
2. In general the quality of ID coating is not as good as standard OD coating, especially in terms of the higher porosity typical of ID coatings.
3. Blind holes are more difficult to spray because the overspray (particles that are not fully softened and bounce off the surface) creates a "dust storm" inside the hole, embedding unmelted particles into the coating and increasing its porosity. This problem is not serious for through holes since particles tend to be swept out in the gas stream. It is also not a problem for HVOF since the gas flows are much higher and the holes larger in diameter.
4. The bottoms of blind holes cannot be coated, except with the use of an angled spray gun head. Most heads only allow coating at right angles to the axis.
5. Because the coatings are more porous, high pressure gas can leak through the coating beneath the seal, making them unsuitable for use in landing gear main cylinders.
6. The RotoPlasma unit is very heavy (about 100kg) and requires a heavy duty robot to manipulate it, rather than the small robot typically used for thermal spray.

#### **6.3.1.3. Nanophase and small particle thermal spray**

Thermal spray of small or nanophase particles may offer solutions to some of the shortcomings of present-day ID plasma spray coatings, especially coating quality and equipment size.

The recent general materials interest in nanophase materials has expanded to thermal spray. R&D of nanophase thermal spray is being funded at the **University of Connecticut, Rutgers, and the State University of New York at Stony Brook** by Larry Kabacoff of **ONR**. Typically, 20 nm particles are agglomerated into 20 micron particles, which are large enough to be fed and injected in standard plasma spray or HVOF guns. These agglomerates break apart in the plasma or flame, releasing the nanometer powder particles. **DARPA** is funding development work at **Northwestern University** on small particle plasma spray (SPPS)<sup>2</sup>, in which the particle size is generally in the 1- 10 micron range. These particles require special feeders and injectors to place them into the outer regions of plasma, where they will be heated correctly. (Particles entering the core of the plasma are overheated and vaporized.)

<sup>2</sup> Grant # MDA972-93-1-0006, "Hard chrome coatings: advanced technologies for waste elimination".

Nanophase and small particle plasma spray coatings are still in the development phase, but results suggest that they are equal to or better than HVOF coatings:

- Small particle/nanophase coatings generally have higher hardness and fracture toughness (higher strain to fracture) than standard coatings.
- They are less porous (similar to HVOF coatings).
- Their adhesion is comparable with that of HVOF coatings.
- Their surface is generally smooth because of the small grain size.

### 6.3.2. Coating materials and properties

A great many materials can be thermally sprayed. HVOF cannot spray most oxides and other ceramics because their melting points are too high, but it can spray most metals, alloys, and cermets such as WC-Co and WC-CoCr. Plasma spray, with its hotter plasma, can spray almost any ceramic, metal, or cermet.

**Table 7. Typical materials properties - thermal spray WC-Co**

| Property                     | Value                   | Notes  |
|------------------------------|-------------------------|--|
| Hardness                     | 1100 - 1400 HV          | Depends on spray conditions  |
| Maximum thickness            | None                    | Usually limited by cost to 0.020"  |
| Corrosion resistance         | Similar to Cr           | Somewhat better than hard chrome, but not as good as hard chrome with Ni underlay. Depends on thickness. No microcracks as-deposited |
| Wear resistance              | 2 - 3 times hard chrome | Smooth surface finish important  |
| Lubricity                    |                         | Not known  |
| Porosity                     | 1% - 5% HVOF            | Higher for plasma spray  |
| Stress and effect on fatigue | Compressive, usually    | Little or no fatigue debit in steels, some debit in aluminum.  |
| Hydrogen embrittlement       | None                    | Even when using hydrogen as fuel   |

### 6.4. Capabilities and limitations

Thermal spray coatings are heavily used in the aircraft (especially turbine engine) industry for both OEM and maintenance applications. The primary capabilities and limitations of the method are summarized in Table 8.

**Table 8. Thermal spray capabilities and limitations**

| Application         | Capabilities   | Limitations   |
|---------------------|--|---|
| Substrate materials | Can be used on most steels and aluminum alloys   |   |
| Outside surfaces    | Rapid coating of large items and areas. Typical coating time 15 mins per landing gear piston (> 60 sq in/min).                     | Line-of-sight. Adequate spray distance (stand off).         |
| Inside surfaces     | 1.5" minimum plasma spray ID, 11" minimum HVOF ID. Smaller IDs can be coated to a depth of 1 or 2 diameters from outside the hole. | Heat dissipation. Removal of overspray for coating quality. |

### 6.5. Other issues

Beside the coating method and properties, other issues are critical to use of thermal spray coatings in OEM and O&R. Some of the most important issues are summarized in Table 9.

**Table 9. Other issues for thermal spray coatings.**

| Item                      | Comment   |
|---------------------------|---|
| Stripping                 | Chemical stripping easy for WC-Co and WC-CoCr. Can be very difficult for some coatings, such as Tribaloy. HVOF coatings cannot be water-jet stripped.                                 |
| Finishing                 | Plasma spray coatings can chip. Diamond wheel needed for WC-Co. Finish may need to be <8 R <sub>a</sub> (better than chrome). Praxair often specifies vibratory stone superfinishing. |
| Process stability/control | Good. HVOF has wider process window than plasma spray. Strongly dependent on powder properties, requiring careful attention to supply source and reliability.                         |
| Chemical stability        | Good for most materials. Still under evaluation.  |
| NDI                       | Flourescent penetrant and Barkhausen work well. Magnetic particle does not appear to work as well as with chrome.   |
| Installation cost         | \$100,000 - 250,000 for equipment, \$100,000 robot, \$250,000 room  |
| Processing cost           | Moderate - 50% - 150% cost of chrome, depending on application. Elimination of hydrogen embrittlement baking is major saver of cost and time-in-process.                              |

### 6.6. Developments needed

In order to use plasma spray or HVOF to replace chrome on internals we need three primary improvements:

1. Smaller guns that can fit better into smaller diameters and have reduced stand-offs from the surface being coated.

2. Reduction or dissipation of the heat load. On ODs heat is removed by air (or even water) sprays, but in IDs the heat is much more difficult to remove. The best improvement would be to reduce the heat generated in the first place.
3. Higher quality, lower porosity ID coatings suitable for high pressure landing gear main cylinder hydraulics. HVOF coatings meet the requirements, but plasma sprays usually do not.

Today's standard guns and powders are inadequate on all of these counts. 1 and 2 above could both be improved by the development of smaller guns. At this point plasma spray guns are almost small enough for deposition on all critical IDs, while HVOF guns remain far too big for almost any ID expected on the JSF. Both HVOF and plasma spray guns could doubtless be reduced in size, but there is a fundamental limitation imposed by the need to have enough space to accelerate and heat the particles adequately.

The use of smaller guns risks making 3 above more difficult to attain - again because of powder velocity and heating rate limitations. Because small particles have lower thermal mass (requiring less energy to heat them) and a higher surface area/volume ratio (permitting more efficient heating in the plasma) it ought to be possible to design smaller guns for spraying small particle powders. These guns would dissipate less energy (less heat removal needed) and permit a smaller stand-off (smaller gun to surface distance). Such guns should fit within smaller diameters and would probably produce higher quality coatings than those typical of today's ID guns and standard powders.

Simple physics allows us to determine roughly how powder temperature and velocity depend on particle size and spray distance (see box). **We find that, as we reduce the powder size, we can reduce the spray distance while maintaining particle temperature and velocity.**

Kinetic energy = Drag force X Spray distance

$$\left(\frac{1}{2}\right) \rho_{\text{powder}} \left(\frac{4}{3}\right) \pi r^3 v_{\text{powder}}^2 = \left(\frac{1}{2}\right) \pi r^2 \rho_{\text{gas}} v_{\text{gas}}^2 D$$

for  $v_{\text{gas}} \gg v_{\text{powder}}$ , where  $\rho$  is the density (of the gas or particle),  $r$  is the powder diameter,  $v$  is the velocity (of the gas or particle), and  $D$  is the stand-off distance.

This leads to

$$v_{\text{powder}} = \sqrt{\left\{ (3\rho_{\text{gas}} v_{\text{gas}}^2 D) / (8\rho_{\text{powder}} r) \right\}}$$

$$\text{i.e. } v_{\text{powder}} \sim \sqrt{(D/r)}$$

Thus, as the particle becomes smaller, the spray distance can be reduced while maintaining the same velocity.

Similarly, for a particle being heated through its surface, by contact with hot gas and absorption of radiation, we have:

$$\begin{aligned} \text{Heat input} &= 4J\pi r^2 \\ &= \rho_{\text{powder}} \left(\frac{4}{3}\right) \pi r^3 C \Delta T / \Delta t \end{aligned}$$

where  $J$  is the heat flux per unit area per second,  $C$  is the specific heat of the powder, and  $\Delta T / \Delta t$  is the rate of temperature rise of the powder particle.

This leads to

$$\Delta T = (3J) / (\rho_{\text{powder}} r C)$$

$$\text{i.e. } \Delta T / \Delta t \sim 1/r$$

Thus, as the particle becomes smaller, its temperature rises more rapidly.



However, if we are to use small powders reliably, several developments will be needed:

1. The gun and powder must be matched to ensure that the powder is adequately heated without being vaporized.
2. A reliable method must be found to feed the powder into the gun. Present day powder feeders can feed powder down to 10 $\mu$ m particle size, and in some cases down to 1 $\mu$ m. This is likely to be sufficient, provided small powders can be made with good flow characteristics (primarily a function of particle shape). If we need smaller particles new commercial powder feeders will be needed.
3. The alternative is to use agglomerated nanopowders, such as the nanophase WC-Co sold commercially by Nanodyne, which can be fed with a standard commercial powder feeder. The question with these powders is how quickly and reliably they would break apart in the plasma, and whether their break-up would be complete, and rapid enough to permit proper particle heating in the limited space between gun and wall. As in 1 above, the powder and gun will need to be properly matched.

## **6.7. Recommendations**

**For the widest use at both the OEM and O&R levels we recommend the development of ID plasma spray, which will require the development of smaller plasma guns and methods for spraying smaller particles.**

### **6.7.1. HVOF**

In many ways an ideal solution would be to reduce the size of HVOF equipment to permit a miniature gun to fit within a 1" ID tube. The gun need only carry gas and a coolant (air or water) and the gas flow could be made as small as desired. The problem, however, is that a minimum stand-off (gun-to-substrate distance) is required to soften the powder and accelerate it to a high enough velocity. While the size of the gun could be significantly reduced, at this point the HVOF equipment manufacturers are not in a position to be able to meet the requirements for ID HVOF coating down to 1" ID from the current 11" ID.

Therefore, we do not recommend HVOF as a viable ID coating technology.

### **6.7.2. Plasma spray**

The advantage of plasma spray over HVOF is the higher energy density in the plasma, which makes it possible to heat the powder rapidly in a small distance. The disadvantages of plasma spray are the bulk of the current equipment (necessitated by the need to carry a large arc current sufficient to be self-sustaining), and the lower quality of plasma coatings (especially their porosity, which prevents their use in high-pressure hydraulic landing gear). On the other hand, existing plasma spray equipment can already be used in diameters as small as 1.5", and new developments in small and nanoparticle thermal spray are producing much better material that would be easier to spray with a smaller gun (since current guns tend to vaporize the material). Furthermore, small particles produce much smoother coatings that may eliminate the need to grind IDs, producing a large saving in cost and manufacturing complexity.

Discussions with equipment manufacturers and thermal spray experts indicate that a combination of a miniaturized plasma gun and small or nanosized powder could well permit the technology to be used reliably down to diameters of 1" ID.

Plasma spray would also fit well with the depots, more of whom have plasma spray equipment than HVOF equipment.

IDs 3" and above can already be plasma sprayed commercially, and are likely to work for many wear applications and lower pressure hydraulics. However, for high pressure landing gear

hydraulics, small or nanoparticle plasma spray will need to be developed to reduce porosity and leakage. (Note that is only on gas-over-fluid landing gear hydraulics, where IDs are generally large and gas leakage must be prevented, that porosity is such a critical issue. Actuators, which are much smaller in diameter, operate at lower pressure and do not have such critical requirements.) This would make the method efficient for coating even the largest ID components, such as landing gear pistons and actuators. **This would account for most of the ID chrome usage in aircraft, especially in landing gear.**

ID plasma spray is likely not to be completely universal, however. The presence of a high temperature plasma source inside an ID will inevitably lead to significant wall heating, becoming more serious the smaller the ID. The heat will be minimized by the lower power of the miniature gun, and high pressure cooling gas will carry away both the excess heat and unmelted particles (which is especially critical in blind holes). However, for smaller IDs in heat-sensitive alloys, such as 7075 aluminum (which is commonly used for landing gear and hydraulic parts) plasma spray may not be possible, even with a miniature gun. This may leave a small percentage of components that cannot be processed by thermal spray.

For the JSF, however, the better solution is likely to be designing those few (if any) components to avoid the need for ID coating, e.g. by choosing a different alloy. Today's components are designed to use chrome, and to take its limitations into account. There is no reason why tomorrow's components cannot be similarly designed to use thermal sprays, taking their limitations similarly into account.

At this point we have no reliable estimates of the reduction in chrome plating by the use of plasma spray technology. From the components we have evaluated and seen in O&R shops we estimate, very roughly, that plasma spray could be used to coat more than 90% of the IDs. Given that IDs are 20 - 30% of the total, this would mean that more than 97% of normally chromed components could be coated by thermal spray. However, since these small IDs require less chrome, this would eliminate more than 97% of the chrome mass deposited for IDs. Together with better materials for those situations where thermal spray cannot be used, this approach would eliminate chrome plating in its entirety.

## **7. Process Summary - Electroplating**

## 7.1. Introduction

The obvious drop-in replacement for hard chrome plating is another, cleaner electroplating technology. There are a number of alternative technologies, including:

- Trivalent chrome - deposition of hard chrome with relatively benign trivalent solutions
- Molten salt bath electroplating - non-aqueous electroplating
- Alloy and composite electroplating - incorporating alloying elements or hard particles into a softer, non-chrome matrix
- Brush plating - local deposition with a pad rather than a large tank.

Since a parallel technology study is presently being done by CTC for Wright Labs, concentrating on electroplating, we will not repeat the same information here. Our general concern with electroplating is that, although it is cleaner than traditional hard chrome plating, it still involves significant environmental, personnel safety, and waste volume issues that non-plating methods avoid.

Most of the electroplating processes are very similar to chrome plating. However, there are a number of composite electroplates that incorporate particles of hard materials such as carbides or oxides to enhance the hardness of the coating. Some of the broad plating technologies are described below.

**Table 10. Summary information - Electroplating**

|                              |  |
|------------------------------|--|
| <b>Process name</b>          | Electroplating   |
| <b>Description</b>           | Deposition from solution - tank and pad  |
| <b>Coating materials</b>     | Metals, alloys, composites   |
| <b>Temperature</b>           | Less than 100C   |
| <b>Minimum ID</b>            | < 1"   |
| <b>Maximum depth</b>         | Unlimited (more problematic for composites)  |
| <b>Stage of development</b>  | Production; some methods in limited or niche production  |
| <b>Primary advantages</b>    | Direct drop-in<br>ID coating relatively simple<br>Composites offer large range of coating design, including hard and lubricious coatings                           |
| <b>Primary disadvantages</b> | Most hard electroplates Ni-based (EPA-17 material)<br>Generally high levels of contaminated waste and rinse water<br>Composites especially difficult to use in O&R |

## 7.2. Process Description

### 7.2.1. Trivalent chrome plating

Under the EPA's Clean Air Act rules trivalent chrome plating is subject to significantly less stringent regulation than the hexavalent process, since it does not produce a hexavalent mist. The primary mist elimination method is a surfactant additive that prevents the formation of large bubbles on the liquid surface, and the primary test method is measuring the surface tension. Traditionally trivalent chrome has only been used for decorative coating because deposition is slow and self-limiting to less than 0.001" in thickness. (It is interesting to note that the German Umweltbundesamt actually prefers hexavalent chrome plating, considering it is easier to control emissions and institute zero-discharge processes for the hexavalent method than to deal with the wastewater issues associated with a trivalent process that uses chelating agents to hold chemicals in solution.)

Recently there has been significant progress in devising methods to make the trivalent method faster and trivalent chrome coatings thicker. None have yet gained market acceptance.

Both Chris Johnson of NIST<sup>3</sup> and M. El-Sharif of Glasgow Caledonian University<sup>4</sup> have developed trivalent chrome solutions that appear to overcome the thickness and deposition rate limitations.

Faraday Technology Inc. has combined the new NIST trivalent plating solution with a pulse plating method (rather than the traditional DC plating method) into a commercial trivalent chrome process<sup>5,6</sup>. The shape of the current pulses is critical to the proper operation of the process. Normal electroplating would use a DC cathodic bias on the substrates. The pulse method gives a long cathodic pulse to plate the Cr, followed by a short anodic pulse to convert the nascent hydrogen produced during the cathodic pulse to molecular hydrogen, which maintains a low pH and prevents the precipitation of chromic hydroxide, which would slow the deposition rate. This process has a deposition rate of about 3 mils/hr (similar to or higher than is typical of hard chrome). The current efficiency for this process is about 35% instead of the 15% typical of hexavalent hard chrome plating.

The chemistry of the Faraday Technology baths is given in Table 11.

**Table 11. Faraday Technology Cr<sup>3+</sup> electroplating bath chemistry.**

|  |          |
|--|----------|
| CrCl <sub>3</sub> .6H <sub>2</sub> O                   | 125 gm/l |
| KCr(SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O | 25 gm/l  |
| NH <sub>4</sub> NH <sub>2</sub> SO <sub>3</sub>        | 178 gm/l |
| NH <sub>4</sub> Cl                                     | 80 gm/l  |
| H <sub>3</sub> BO <sub>3</sub>                         | 30 gm/l  |
| HCOOH  | 30 ml/l  |
| pH   | 2        |
| Temperature  | 20 - 60C |

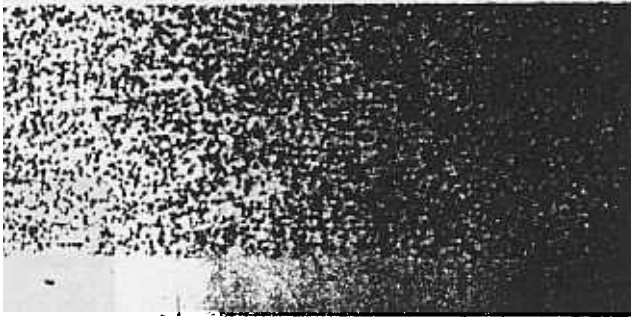
<sup>3</sup> US Patent # 5,415,763 (1995): "Methods and electrolyte compositions for electrodepositing chromium coatings".

<sup>4</sup> M. El-Sharif, 18<sup>th</sup> AESF/EPA Pollution Prevention and Control Conference Proceedings, Orlando (1997), p 143.

<sup>5</sup> US Patent # 5,196,109 (1993): "Trivalent chromium electrolytes and plating processes employing same".

<sup>6</sup> Renz et al., 18<sup>th</sup> AESF/EPA Pollution Prevention and Control Conference Proceedings, Orlando (1997), p 115.

### 7.2.2. Composite electroplating



**Figure 19. Tribomet T104CS coating cross section. 200x**

There are various types of composite electroplate, which incorporate small diameter powder into the coating. Recently both Boeing and McClellan AFB (Elwin Jang) tested the proprietary Takada process for chrome replacement of items such as hydraulic pistons. This plating method uses SiC particles in a Ni-W matrix. After extensive testing the method was abandoned as too difficult to use reliably in production.

Praxair has a proprietary composite electroplate, with the tradename of Tribomet®, which comprises a high

percentage of 4 - 8  $\mu\text{m}$   $\text{Cr}_3\text{C}_2$  particles in a cobalt matrix<sup>7</sup>. There are two formulations - T104, with 10 - 25 wt%  $\text{Cr}_3\text{C}_2$ , and T104CS, with 30 - 40 wt%  $\text{Cr}_3\text{C}_2$  (see Figure 19). These materials are designed for high temperature turbine engine use, and are specified to require a 900C heat treatment, which greatly increases the hardness and forms an oxidation-resistant cobalt oxide glaze on the surface.

As-deposited Tribomet coatings are quite soft - 300 HV for T104C and 450 HV for T104CS, compared with 800 - 1,000 HV for hard chrome. After high temperature annealing the T104CS reaches 750 HV. Tribomet can be used on IDs down to 9.5 mm (0.375") diameter by the use of an internal anode.

### 7.2.3. Alloy electroplating

While most electroplates are elements (Ni, Cr, etc.) it is possible to create wear-resistant surfaces by using alloys such as Ni-W-B, Co-W, W-Co-B, or Ni-W. The boron-containing materials tend to be amorphous<sup>8</sup>. Most of these alloy electroplates are available commercially, but from a limited number of vendors. Boeing is currently investigating the use of alloy rather than composite electroplates in order to avoid some of the problems posed by suspending particles in the plating solution.

A recent modification of this approach is multilayer alloy plating<sup>9</sup>, which is the electroplating analog of nanolayer PVD coating. The idea behind this approach is that interfacial interactions between layers of different materials can produce much harder, more wear-resistant coatings than either material alone. The thicknesses of the individual layers must be on the order of dislocation loop dimensions (typically 2 - 20 nm). In order to be able to plate an alloy of this type the constituents must plate out at potentials that differ by at least 100 mV, and plating is usually done by current or voltage pulsing. (It is possible, of course, to use two baths, but such a method would be highly inefficient.)

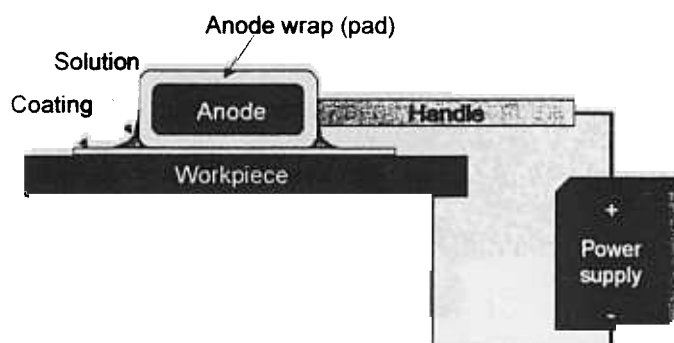
<sup>7</sup> US Patent # 5,558,758 (1994): "Electrodeposited composite coatings".

<sup>8</sup> US Patent # 4,529,668 (1984) "Electrodeposition of amorphous alloys and products so produced".

<sup>9</sup> See, for example, D.T. Schwartz, "Multiple-layer alloy plating", ASM Handbook, Vol. 5, 274 (1994).

### 7.2.4. Brush plating

Brush plating (or selective plating) has been in use for over 30 years in the US and is included in over 100 government, military and industrial specifications. The principle of the method is that the plating solution is held in a pad rather than a tank, and plating takes place only beneath the pad (Figure 20). The head is usually hand-held, although it can be set up for more controlled automatic plating. Brush plating is primarily used for localized manual repair, and can be used to deposit almost



**Figure 20. Brush plating schematic.**

any (non-composite) electroplate, including sulfamate nickel, which is widely used for build-up and repair. It is used in a wide variety of repair and touch-up applications, which range from highly visible large volume uses such as building domes and church steeples (up to 15,000 sq ft of Cu, Ni and Au) to very small such as electronic parts. Because it uses a pad rather than a tank of liquid, it is relatively easy to coat IDs, and masking is not usually an issue. While the volume of brush plating solutions is very small compared with large tanks of chromic acid, the solutions tend to be more concentrated.

Industrial applications include rotogravure rolls and other printing rolls, molds for plastics manufacture, printed circuit boards, steel mill coating lines, and bearing and seal surfaces in turbines. Aerospace and military applications include space shuttle manifolds, missile launch rails, aircraft engine components, aircraft landing gears and wheels, and aircraft exterior skins.

**Table 12. Summary information - Brush plating**

|                              |   |
|------------------------------|---|
| <b>Process name</b>          | Selective Plating/Brush Plating   |
| <b>Description</b>           | Selected area electroplating in which the plating solution, or electrolyte, is portable and brought to the area to be coated using a handheld stylus. The workpiece is the cathode, the stylus the anode.   |
| <b>Coating materials</b>     | Most metals but particularly Cd, Co, Cu, Cr., Ga, Au, In, Ir, Fe, Pb, Ni, Pd, Pt, Rd, Ag, brass, bronze, Co alloys, Tin alloys  |
| <b>Temperature</b>           | <100C   |
| <b>Minimum ID</b>            | At least as small as for Cd touchup in ID of oil air strut on landing gear accommodating press fit of a bronze bearing  |
| <b>Maximum depth</b>         | Unlimited   |
| <b>Stage of development</b>  | Commercially available  |
| <b>Primary advantages</b>    | Portability; higher deposition rate (than bath plating); precise thickness control; post-machining not required on thicknesses up to 0.254 mm (on a smooth substrate); can also perform other related functions such as electrostripping, anodizing, electromilling, electroetching, electropolishing |
| <b>Primary disadvantages</b> | Limited adhesion for titanium, tantalum and tungsten; need conductive substrate   |

### 7.2.5. State of development

Most of the simple bath and brush electroplating methods are in commercial use. The main exceptions are:

- trivalent chrome, which is still in the development and validation stage, and has not yet come into commercial use,
- layered alloy plating, which is quite new and complex to use, and
- hard alloy plating, which is available commercially, but in a limited way.

### 7.3. Coating materials and properties

Because of the wide variety of coating materials that can be electrodeposited, the properties are very broad.

**Table 13. Typical materials properties - Electroplating**

| Property                     | Brush plating                               | Tribomet   | Trivalent chrome                   |
|------------------------------|---|--|------------------------------------|
| Hardness                     | 250 to 575 HV for sulfamate nickel coatings | 300 HV, 450 HV as-deposited; 750 HV heat treated | 700 - 850 HV                       |
| Maximum thickness            | up to 0.030"                                | 0.030"   | 0.020"                             |
| Corrosion resistance         | good  | -  | similar to EHC                     |
| Wear resistance              | good  | similar to plasma Tribaloy and EHC               | similar to plasma Tribaloy and EHC |
| Porosity                     | 25% less porous than EHC                    | -  | similar to EHC                     |
| Adhesion                     | very good most alloys, poor for Ti, W, Ta   |  |                                    |
| Stress and effect on fatigue | unknown                                     | unknown  | unknown                            |
| Hydrogen embrittlement       | Yes   | unknown  | unknown                            |

### 7.4. Capabilities

The clear advantage of electroplating methods is that they are closest to a "drop-in" replacement for chrome plating. They can be used for IDs by the use of rod anodes placed into the ID. Tribomet, for example, can be used on IDs down to 0.375" by using an internal anode. While many of the electroplates are nickel-based, electroplates such as Co-W, W-Co-B, and Tribomet avoid the use of EPA-17 materials.

Selective plating is often used for hardfacing repair, usually with Cr or an alloy such as Co-W. It is used primarily to electroplate small areas of large parts, parts that are too large to immerse in plating tanks, and for repair or touch up on any size components that are expensive to strip for full tank immersion. The strongest advantage of the brush or selective plating process is the avoidance of masking, which is a large part of the total plating cost, primarily because of the labor time involved.



## 7.5. Limitations

**Rinse water and waste volumes** - All aqueous plating processes involve the use of copious amounts of rinse water to remove electroplating solution. There is always some drag-out from plating tanks, except in the case of brush plating, where the item is not put into a tank.

**Materials** - All electroplates that are based on Ni have serious environmental and worker safety concerns since Ni is an EPA-17 material.

**Composite coatings** - In order to match the hardness and wear resistance of chrome, most electroplates require the addition of hard particles. All composite coatings, including Takada and Tribomet, have the problems inherent in using particles in a plating process (also discussed under "Electroless Nickel"). Boeing has found that it is extremely difficult to maintain the particles in the proper concentration throughout the bath in the production environment. This leads to variable properties, especially over large or complex objects. Furthermore, when the tank is not in use the particles tend to settle and cannot be put back into suspension. This is an especially serious problem for the O&R environment, where production tends to be sporadic. We expect that this problem is likely to be more difficult with blind holes, where powders may deposit in dead spaces or may not properly reach some internal areas. Composites generally require heat treatment to achieve good hardness, which also limits their usefulness (see below).

**Tribomet** - As-deposited the coatings are quite soft (up to 450 HV). The treatment needed to increase the hardness to that of EHC involves heat treatment at 900C, which is too high for most structural materials. It is possible that these coatings can be used without the heat treat, but at this time no information is available on their performance.

**Brush plating** - Parts with complex geometries can be plated faster and more efficiently using tank coatings. The method does not lend itself well to the efficient plating of small components. Large numbers of small parts are better plated using barrel plating. It is difficult to obtain adhesion on Ti alloys, which are frequently used in newer landing gear.

**Trivalent chrome** - The process is as yet too new to have solid information on producibility and performance. It is likely that trivalent plating of aluminum will pose the same difficulties that are encountered with hexavalent chrome solutions, where adhesion is very unreliable. Trivalent solutions avoid the serious problems of air emissions, but they do not avoid the problems of disposal of stripping solutions or worker exposure to chrome dust during grinding.

**Heat treating** - Most composite coatings seem to require heat treatment to reach acceptable hardness levels. As with electroless nickel this limits their use on heat sensitive structural alloys. The problem is especially acute with Tribomet, which requires a 900C heat treatment, although it is possible that performance would be adequate without the heat treatment.

**Hydrogen embrittlement** - Hydrogen embrittlement is a concern for all aqueous plating processes, since they tend to release nascent hydrogen at the substrate. While the hydrogen can be removed by heat treating, this raises the cost of the coating process, especially for large components such as landing gear.

## 7.6. Fit with OEMs and depots

The basic fit of electroplating processes (especially bath plating methods) with OEMs and depots is very good. The details of tank chemistry and operation will differ, of course, from that of hard chrome, but most operations are familiar with a number of different plating baths.

However, the composite coatings have some significant problems that would limit their usefulness, especially in the depots, which have been discussed in Section 7.5 above. The primary concern over settling out of particles from the bath is especially acute in the depots, where production is less continuous. The particles must be continuously held in solution.

## 7.7. Developments needed

If composite coatings are to be brought to production, simple and reliable methods will need to be found to maintain the particles in suspension during periods when the plating bath is not in use. In principle this is not a serious problem since it should simply require that the bath continue to be agitated at all times. Even with this, however, some material is likely to drop out of suspension, especially in "dead areas" where there is little movement of the fluid, and this will slowly deplete material from an unused tank.

Uniformity of particulates throughout the bath, and especially inside blind holes and other difficult areas will need to be ensured by proper agitation and/or direction of fluid flow. It will be important to ensure that particulates remain uniform within holes (especially within blind holes) and do not drop out of suspension in dead areas of the component (including areas where plating is not desired).

Methods will need to be developed to measure and maintain particle concentration throughout the bath, both to ensure uniformity and to ensure that the bath is still usable after quiescent periods.

Many composite coatings require heat treatments at temperatures that are too high for most structural alloys. Whether or not these heat treatments are really needed, or whether they can be done at lower temperatures needs to be determined. An alternative is to develop heat treating methods that affect only the coating, such as laser or flash lamp methods. In order to avoid overheating the substrate, most of these methods allow only momentary heating, however, which is unlikely to permit the extensive diffusion and precipitation that seems to be required.

## 7.8. Recommendations

Of the electrodeposition methods the most viable would appear to be trivalent chrome and composite coatings. Trivalent chrome is an obvious drop-in alternative, while the various hard alloys and composites would appear to be the only coatings that offer equivalent or superior performance to hard chrome.

**Trivalent chrome** - Of the different plating methods trivalent chrome is the obvious drop-in replacement for hexavalent chrome. However, it is too early to know how well it will perform or what production processing will really be like. It also has the same environmental and worker safety issues as hard chrome in the grinding and stripping processes. **Therefore it is not recommended.**

**Alloy plating** - Some of the alloys look quite promising. Boeing, for example, is beginning to investigate the use of alloys such as Ni-W as ID chrome replacements. Again, Ni-based materials are probably best avoided. However, this does leave Co-based alloys such as Co-W and Co-W-B. These alloys avoid the problems inherent in composite electroplating. **We recommend that alloy plating be evaluated, provided that the chosen alloy solution does not contain nickel or itself pose serious environmental or worker safety concerns.**

**Composite plating** - Given the poor experiences with composite plating from Boeing we do not believe that it is a viable replacement at this time, especially for depot use, where the production problems are likely to be more serious than at the OEMs. However, since composites provide a high level of flexibility to electroplating, allowing us to design very wear resistant or very hard electroplates, it would be worthwhile evaluating how the problems of dealing with suspended particles might be overcome, especially at the depot level.

## **8. Process Summary - Electroless nickel**

## 8.1. Introduction

**Table 14. Summary information - electroless nickel.**

|                              |  |
|------------------------------|--|
| <b>Process name</b>          | Electroless nickel plating   |
| <b>Description</b>           | Autocatalytic deposition of Ni with up to 11% P or B without use of electric current   |
| <b>Coating materials</b>     | Ni-P, Ni-B. Sometimes SiC, diamond, PTFE, other particles added to form composites   |
| <b>Temperature</b>           | 10 - 90C deposition, 300 - 400C heat treatment   |
| <b>Minimum ID</b>            | None   |
| <b>Maximum depth</b>         | None   |
| <b>Stage of development</b>  | Commercial. Composite coatings less fully commercialized   |
| <b>Primary advantages</b>    | Fully commercial<br>Existing commercial and MIL specs for aircraft   |
| <b>Primary disadvantages</b> | Ni is a Toxic-17 material<br>Sensitivity to bath chemistry - difficult to control<br>Finite bath life - spent bath must be disposed as toxic waste<br>Hydrogen embrittlement |

Electroless nickel is a well-defined commercial process available in commercial shops and DoD depots. Because the process is very sensitive to bath chemistry, temperature, and contamination experience with it is somewhat spotty, with some aerospace companies (such as Boeing St Louis) using it on a regular basis and others (such as Pratt and Whitney) regarding it as unacceptable. Because Ni is also on the EPA "Top 17" list, there is a wide divergence of opinion for and against its use.

In its Statement of Needs<sup>10</sup>, San Antonio ALC states

*"Electroless nickel deposits can achieve either excellent wear resistance or good corrosion protection by varying the amount of phosphorus or boron in the coating. Because nickel has been identified as an EPA 17 hazardous chemical, it would be advantageous to identify an alternative coating."*

In discussing chrome plating alternatives, Brooks AFB<sup>11</sup> states

*"Electroless nickel is advertised as a potential replacement for chromium. We do not like electroless nickel due to the difficulty in maintaining the bath, the slow plating rate, the frequent bath disposals required, and the difficulty in stripping nickel when the parts return for overhaul. Potential substitutes are nickel-tungsten-silicon carbide electroplating, high energy thermally deposited coatings, and a proprietary process call Amplate which is a nickel-tungsten-boron electrodeposit."*

<sup>10</sup> #617 HMRPP

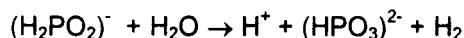
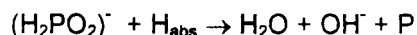
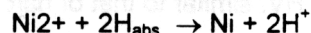
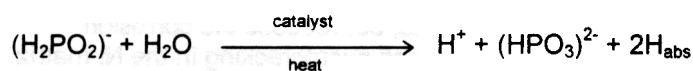
<sup>11</sup> Statement of Need #251

Amplate is also, of course, a nickel-based alloy. An electroplate called the Takada process, which is similar to Amplate, but with SiC additions, has been tested as a chrome replacement by Boeing and at Sacramento ALC, but rejected due to difficulties in scale-up.

There is a strong divergence of opinion on the usefulness of electroless nickel even absent concern over environmental issues. Most of this divergence appears to result from the different experiences of users. For example, Boeing Commercial avoids electroless nickel, while Boeing Defense uses it quite heavily; Messier-Dowty considers it expensive and unreliable for landing gear, while Heroux uses it quite extensively.

## 8.2. Process description

Nickel is deposited by the autocatalytic chemical reduction of nickel ions onto the surface of the part without the use of electric current. In the most common type of bath, the hypophosphite bath (used to deposit Ni-P), the chemical reaction sequence is believed to be<sup>12</sup>:



In the first reaction hydrogen is evolved at the surface of the part being plated, some of which is absorbed at the surface. This hydrogen reduces Ni ions at the surface, depositing Ni metal, and reduces some of the hypophosphite to deposit phosphorus. Most of the hypophosphite is oxidized to orthophosphite, with evolution of more hydrogen.

Electroless nickel solutions typically contain the following types of materials:

1. A source of Ni (usually Ni sulfate)
2. A reducing agent
3. Complexing agents (chelators) to control the amount of free nickel
4. Buffering agents to maintain the pH
5. Accelerators to increase the reaction rate
6. Inhibitors to control reduction reactions

The most commonly used hypophosphite bath typically operates at a temperature of about 90C. As the reaction proceeds, byproducts such as orthophosphites build up in the bath and interfere with the deposition.

Instead of hypophosphite, the bath can be based on aminoborane or borohydride, which creates Ni-B. These baths operate at lower temperatures and produce coatings of higher as-deposited hardness, but typically lower corrosion resistance due to increased crystallinity.

There are numerous composite coatings based on electroless nickel containing particles such as SiC, diamond, or PTFE to provide better hardness or lubricity.

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<sup>12</sup> ASM Handbook, Vol 5 (1996)

### 8.2.1. State of development

Electroless nickel has been in commercial use since the 1950's. It is widely available commercially, most commonly as Ni-P, but also as Ni-B and as electroless nickel composites. Many of the DoD repair depots and aerospace manufacturers have electroless nickel capabilities and there are a number of commercial and MIL specs for these coatings, such as AMS 2404C and MIL-C-26074E.

Many aerospace suppliers and depots are experienced with electroless nickel.

### 8.2.2. Coating materials and properties

#### Ni-P

In NiP the phosphorus can vary from less than 1% to about 11%. As-deposited, the material has a hardness of about 500-600 HV (48-52 HRC). The material has good corrosion and wear resistance, but both properties depend strongly on the heat treatment. Heat treating above 220C precipitates nickel phosphide, which increases the hardness, but reduces the corrosion resistance because of its introduction of grain boundaries and microcracking in the Ni matrix. Heat treating at 400C for an hour raises the hardness to 1000-1100 HV, similar to that of hard chrome, but reduces the corrosion resistance by a factor of 100.

The deposition rate is typically about 1mil/hr (comparable with chrome plate), which falls as the bath ages.

#### Ni-B

Ni-B is less widely used as it appears to be more difficult to deposit. It is harder as-deposited, and can be harder still after heat-treating, when Ni boride precipitates. However, the material is not amorphous, and is consequently generally less corrosion-resistant as-deposited. It can assume a nodular form which gives it a lower contact area and lower friction (Cemkote).

**Table 15. Typical materials properties - electroless Ni**

| Property                     | Value                   | Notes   |
|------------------------------|-------------------------|---|
| Hardness - Ni-P              | 500 - 700 HV            | as-deposited  |
|                              | 900 - 1,100 HV          | after 400C heat treatment   |
| Hardness - Ni-B              | 650 - 750 HV            | as-deposited  |
|                              | up to 1200 HV           | after 400C heat treatment   |
| Maximum thickness            | >10 mils                | 1 mil typical for corrosion service   |
| Corrosion resistance         | 0.6 - 50 mil/yr         | 10% HCl, depending on heat treat, from none to 400C                                   |
| Wear resistance              | Good                    | If heat treated, similar to chrome  |
| Lubricity                    | Good                    | Similar to chrome   |
| Porosity                     | Low                     | As-deposited is usually non-porous. Microcracks on heat treating                      |
| Stress and effect on fatigue | Variable to detrimental | Usually tensile, become more tensile on heat treat. Would tend to reduce fatigue life |
| Hydrogen embrittlement       | Yes                     | Hydrogen evolved during deposition  |

### 8.3. Electroless Ni composites

There are a great many electroless nickel composite coatings, obtained by incorporating particles into the Ni layer. The advantage of composites is the ability to build in better lubricity or hardness. Their disadvantage is the added complexity, especially in maintaining uniform deposition of the particles in complex and internal geometries.

Commercially available composite coatings contain either diamond, silicon carbide, tungsten carbide, chromium carbide, boron carbide, aluminum oxide or PTFE particulates. Maximum particle size for most composite coatings is 10 microns. The primary goal behind the additives is to enhance existing electroless nickel properties.

The additives are generally insoluble particulates codeposited with the electroless nickel coating. Particulate matter stabilizers (pms) must be added, in precise amounts, to avoid incompatibility between the plating bath, which is inherently unstable and surface-area dependent, and the high loading of insoluble particulates. Stabilizer technology is described in US patents 4997686; 5145517 and 5300330. Particle densities of up to 40% by volume can be produced, but densities of 15 -25% are suitable for most applications. Each type of particle requires different bath parameters to optimize coating properties.

Because the particulates are fairly uniformly distributed throughout, composite electroless nickel coatings are considered to be regenerative - i.e. their properties are maintained as the coating wears down. Although most composite coatings contain micron-size particles, some development work is also being done with nanoparticles. Particle shape is also a consideration when designing optimum coatings and deposition conditions. Typically, coating thicknesses range from about 7 to a maximum of 50 microns, with most coatings in the 12 to 25 microns range. Some general properties for several types of composite EN coatings are summarized below:

**Table 16. SiC composite electroless nickel (SiC-EN)**

| Property                             | Value                                |
|--------------------------------------|--------------------------------------|
| hardness                             | 1200 VHN (after heat treatment)      |
| thickness                            | 0.001 to 0.003 inches                |
| coefficient of friction              | 0.42 (EHC is 0.43; EN is 0.47)       |
| wear resistance                      | 3 times more wear resistant than EHC |
| abrasion resistance (std Taber test) | minimal weight loss                  |

**Table 17. PTFE composite electroless nickel (PTFE-electroless nickel)**

| Property                        | Value  |
|---------------------------------|--|
| hardness (as-deposited)         | 250 HV   |
| hardness (heat treated)         | 400 HV   |
| thickness                       | 0.2 - 1 mil (6 to 25 microns) for lubricity and good release;<br>0.5 - 2 mils (13 to 50 microns) for corrosion resistance                              |
| corrosion resistance            | non-crystalline microstructure provides corrosion resistance. 1 mil thick coating demonstrates salt spray resistance 500-1000 hrs per ASTM B-117 tests |
| wear resistance                 | good - PTFE provides lubricity, HT hardness provides good wear/abrasion resistance   |
| friction coefficient (vs steel) | 0.1 - 0.3  |

**Table 18. Combined hard, lubricious electroless nickel (PTFE+SiC-EN)**

| Property             | Value   |
|----------------------|---|
| Hardness             | 1000 HV with heat treatment   |
| Thickness            | Variable - dependent on application   |
| Corrosion resistance | Superior to hard chrome; suitable for mild corrosive environments. 1-mil thick coating demonstrates salt spray resistance 700 hrs per ASTM B-117. |

**Table 19. Diamond composite electroless nickel (Diamond-EN)**

| Property  | Value  |
|---|--|
| Wear resistance (Taber wear test for heat treated D-EN) | 11.4 cubic mils/hr (compared with 16.5 as-plated and 46.2 for EHC) |
| Wear resistance (DuPont accelerated yarnline wear test) | 1.26 cubic mils/hr (compared with 966.60 for EHC)                  |

Clearly, composite electroless nickel coatings can be designed with a wide range of properties for different applications. For example, the hard composites such as diamond- and SiC-EN can be used for wear applications such as textile fiber guides, spinnerettes, injection mold dies, extrusion dies, and equipment in food processing, paper processing and packaging machinery industries. Lubricious, but softer, PTFE-EN and PTFE+SiC-EN have found applications in hydraulic cylinders (which is of obvious interest in aircraft, since hydraulic actuators and landing gear are the primary applications for hard chrome), bearings, industrial spray nozzles, industrial valves, and components for fuel systems and transmissions.

It should be noted that in general, the corrosion resistance of composite electroless nickel coatings is not as good as that of the standard electroless nickel coatings. The large amounts of occluded materials, or particulates, in the coating reduces alloy passivity and corrosion resistance. For all types of electroless nickel, as-deposited coatings are more corrosion resistant than heat-treated coatings, since heat treating transforms the amorphous deposit to crystalline Ni



and Ni<sub>3</sub>P, and cracking of the coating is more likely. For certain types of composite coatings, the presence of such particulates as diamond or intermetallics exacerbates this problem. The ASM Handbook (V. 5, p 309) points out that the presence of phosphides (from the basic Ni-P EN chemistry), Ni and various particulates, creates a strong galvanic couple that can accelerate corrosive attack in situations where electroless nickel coated and bare metal are in proximity.

#### **8.4. Fit with OEMs and depots**

The fit of electroless nickel and composites with both OEMs and O&R sites is quite good. One of the advantages of the process is that it is a bath process, in common with chrome plating. This makes it familiar to plating shops. However, the electroless nickel process is considerably more complex than chrome plating because of the far higher level of control required by the process. As a practical matter, this need for control often leads to process unreliability (often put in terms of "black art"), which OEMs and depots report as a persistent problem. The proprietary nature of electroless nickel solutions makes it difficult to troubleshoot the process, whether it is done in-plant or with a vendor.

#### **8.5. Typical costs and cost factors**

The cost of electroless nickel on a per-part basis is generally similar to that of chrome plate. Because of the requirement of heat treating for hardness and for embrittlement relief, costs of post-deposition treatment are also similar. Life-cycle cost is likely to be similar - perhaps somewhat higher or lower, depending upon the hardness of the final coating, and its wear resistance in specific applications.

#### **8.6. Advantages and capabilities**

**Uniformity** - Since electroless nickel is not dependent on the use of electric fields, the method gives good uniformity and is ideal for coating inside tubes. Consequently it is often used to plate the insides of cylinders. Coatings can be built up to greater than 10 mils if needed for rebuild. However, deposition rate is quite slow - usually no more than 1 mil per hour (similar to chrome).

**Specifications** - A very strong advantage of electroless nickel is the fact that there are existing commercial and military specifications, making it far quicker and less expensive to adopt than many other technologies. The primary specifications used in the aircraft industry are AMS 2404 and MIL 1501, which are broad specifications rather than detailed methodologies. The existence of these specifications, however, makes the process of acceptance for specific components far easier and quicker than it would be for a completely new process.

**Commercial availability** - Commercial bath solutions already exist from a number of suppliers. However, most of these solutions are proprietary, using a basic chemistry, with proprietary additions. There are a number of vendors who offer the process commercially, albeit far fewer than the number of chrome plating shops. Ni-P is much more readily available than Ni-B.

#### **8.7. Disadvantages and limitations**

**Environmental** - The primary disadvantage is the fact that Ni is also on the Toxic 17 list. Although there is presently far less stringent regulation of Ni, it is generally expected that regulators will turn their attention to Ni once the more serious chrome plating problems are solved.

Electroless nickel baths have a finite life, after which the bath must be dumped and disposed of as toxic waste. The bath life is dependent on how the bath chemistry is maintained and on the materials being processed, but life is usually limited to about 10 metal turnovers. Baths must also be dumped if they become contaminated with certain metals. For chrome replacement the most critical contaminant is likely to be chromium. Sirius Technology, which sells electroless

nickel plating solutions, states that for a low-P bath, 3 ppm of  $\text{Cr}^{3+}$  creates unacceptable deposits, while 0.2 ppm of  $\text{Cr}^{6+}$  stops deposition completely, leading to the need to dump the bath in either case. Given that any existing component being internally plated will have chrome plated surfaces (which might not always be completely stripped), the risk of chrome contamination is high.

**Reliability** - The second major disadvantage is reliability (especially adhesion strength), which seems primarily to be related to the difficulty of maintaining proper substrate cleaning and deposition conditions. The method is very sensitive to bath chemistry and temperature, including bath contaminants. We suspect that this sensitivity is the source of the variable experience reported by different users. Long term process reliability remains an issue that must be treated seriously, especially when the method is to be used in the depot environment where the workload is constituted by large numbers of different components.

The precipitation of phosphides and borides introduces strains into the nickel lattice that can result in cracking, porosity, and consequent premature corrosion. Non-uniform precipitation and segregation has sometimes been found to produce non-uniform hardness, which can create problems in wear applications.

**Technical** - Hydrogen embrittlement of high strength steels is a concern for aerospace users. The deposition process releases hydrogen at the substrate, but unlike chrome, in which microcracks allow the hydrogen to escape, electroless nickel forms a less porous layer, requiring some surface area to be left unplated to allow the escape of hydrogen during heat treating.

As-deposited, Ni-P is relatively soft (500 HV), while Ni-B is harder (750 HV), but still softer than chrome (1,000 HV). Heat treating for hardness will be a problem for many high strength steels and aluminum alloys, especially when treatment temperatures are in the region of 400C for up to 8 hours (Cemkote). (This heat treatment also, of course, eliminates hydrogen to prevent hydrogen embrittlement.) This is not usually a problem for corrosion-resistant use of electroless nickel, since the best corrosion resistance is obtained in the as-deposited form. However, to obtain hardness and wear resistance comparable to chrome, as well as to avoid embrittlement, heat treating will generally be required.

## 8.8. Developments needed

The electroless nickel process itself is fully developed, and has been in use for 30 years, but has failed to gain wide acceptance in the aerospace industry, although it is used for niche products. The primary reason for the failure of electroless nickel to penetrate widely into the aerospace market appears to be the difficulty of maintaining a consistent plating (from comments made by Boeing, Messier-Dowty, and others). Consistency is a problem both among different vendors, and often within a single shop.

**Process control** - Therefore, if electroless nickel is to be used very widely, methods will need to be developed and made commercially available to monitor and control the bath chemistry, temperature, and performance on a continuous basis, as well as to control the heat treatment temperature and time. These cannot be sophisticated laboratory methods, but will have to be suitable for use in the general shop environment of repair depots and manufacturing plants. Some companies have developed computerized methods for production use in their own plants, but these methods are not commercially available.

The use of composites would make such control methods even more important, since one must then control bath chemistry more closely (to prevent deposition onto bath particulates) and one must control the particulates themselves. Methods must be found to maintain the filler powders in a uniform concentration and to obtain proper entrainment in the coating. This is clearly a concern for more difficult geometries such as IDs. Difficulty in maintaining SiC in suspension was the primary reason for Boeing's failure to adopt the Takada process (which is an electroplate with SiC additions).

**Specifications** - Although AMS and MIL specifications (as well as internal prime contractor specifications) already exist, they need to be supplemented with much tighter specifications that will guarantee the properties and consistency of the material. Additional specs will be needed for the various composite electroless nickel coatings.

## 8.9. Recommendations

The primary advantage of electroless nickel is that it is a well-established process, already used by some aerospace OEMs and repair depots, and already demonstrated to be capable of plating inside IDs less than 1" in diameter. It already has aerospace specifications, standards, and repair procedures. It would require very little development, but would require demonstration and validation for JSF parts. Its long history of unreliability with some OEMs and depot engineers would require that its reliability be ensured through proper specification and process control, and clearly demonstrated, not just at a single vendor, but in typical depot overhaul situations.

However, the fact that Ni is on the EPA Toxic 17 list makes it only somewhat less of an environmental problem than hard chrome. Indeed, it is generally expected that Ni plating regulation will become more stringent over the next 10 years or so. This has already begun to happen in California, where the local air quality management district for the Los Angeles area has been deciding whether to regulate nickel plating. NAMF, the National Association of Metal Finishers, has responded with a "Nickel Defense Fund", just as they did earlier with the "Chrome Defense Fund" to alleviate the severity of chrome regulation and minimize its impact on the electroplating industry.

**Because of environmental concerns, we view electroless nickel as at best a stopgap alternative to chrome plating.** If dry alternatives or clean electroplates cannot be put into production early enough to meet JSF's goals, then electroless nickel or electroless nickel composites could be a viable alternative, if approved by JSF engineers. Because of the difficulties of process control, they might be used at the OEM level, but not at the O&R level, since we could presumably have more environmentally acceptable alternatives in place by the time aircraft are returned in great numbers from the field for servicing.

In order for electroless nickel to garner broad acceptance as a chrome replacement it will be essential to overcome its real and perceived unreliability. This might best be done by developing and commercializing production methods for monitoring and controlling surface preparation and bath chemistry. These methods must work in both OEM and O&R environments, and may need to be put into place in conjunction with more chemically stable plating solutions. A number of vendors claim to have more stable chemistries, but these are proprietary. For electroless nickel to be used on the full range of JSF components not amenable to HVOF, these solutions must be available commercially, or equivalent non-proprietary chemistries will need to be developed.

If composite electroless nickel coatings are to be used, control of the particulate distribution will be critical, since this has already proved to be a sticking point in composite electroplating processes.

**Table 20. Summary of developments needed for electroless nickel.**

| Concern                                     | Development needed   |
|---|--|
| Unreliable adhesion and coating properties  | Computerized monitoring and control of substrate surface preparation and bath chemistry.<br>Non-proprietary solution chemistries to enhance stability. |
| Uniform particle distribution in composites | Improved methods to measure and control particle distribution in solution and on the surface.  |

## **9. Process Summary - Chemical Vapor Deposition (CVD)**

## 9.1. Introduction

Chemical Vapor Deposition (CVD) has been used for many years in production for deposition of coatings on externals and internals. It is based on the principle of bringing materials (called precursors) into the deposition area in the gas phase, and breaking them down and reacting them (usually with heat or a plasma assistance) to deposit the coating. Because the material is initially in gaseous form it can penetrate very small and very long IDs. In fact one form of CVD, called Chemical Vapor Infiltration (CVI) is used in production to fill the interstices in fiber composites, where the holes are only microns wide and aspect ratios exceed 100:1. CVD materials can be made extremely thick - e.g. CVD is used to grow ZnS infrared window material several inches thick and several feet in diameter.

CVD can produce a wide variety of coatings, including metals and compounds. However, the thermodynamics of the process generally do not permit it to be used for alloy deposition or for the deposition of composites such as WC-Co.

Most CVD processes are done in a sealed vacuum chamber, with the exception of combustion CVD (CCVD), which can be done in air. The reason for this is that most CVD precursors are toxic and/or dangerous (pyrophoric, highly acidic, extremely reactive with water or oxygen, etc.). Although there are ways of controlling the CVD process, trapping harmful byproducts, and even of closed loop recycling of precursors, the process is not frequently used outside specialist companies with well-trained personnel.

**Table 21. Summary information - CVD**

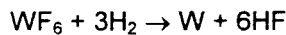
|                              |   |
|------------------------------|---|
| <b>Process name</b>          | CVD   |
| <b>Description</b>           | Deposition by breaking down gas phase precursors using heat or plasma energy  |
| <b>Coating materials</b>     | Metals (e.g. Ni, Ta, W) and compounds (oxides, nitrides, carbides, sulfides), including multilayers. <u>Not</u> alloys or composites. |
| <b>Temperature</b>           | Typically 1,000C with simple precursors, 100-500C with metalorganics (MOCVD)  |
| <b>Minimum ID</b>            | Microns   |
| <b>Maximum depth</b>         | Very large - aspect ratios >100:1   |
| <b>Stage of development</b>  | Production  |
| <b>Primary advantages</b>    | Capable of high thickness, large aspect ratio holes<br>Many different coating materials   |
| <b>Primary disadvantages</b> | Thermal CVD - temperature too high for structural alloys<br>MOCVD - dangerous, often unstable precursors                              |

## 9.2. Process description

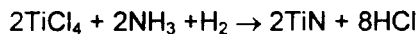
### 9.2.1. Thermal CVD

Thermal CVD is the most widely used method for coating such items as WC-Co metal-cutting inserts, which are capable of withstanding the typical 1,000C processing temperature. A typical arrangement is shown in Figure 21. The substrates in the chamber are usually heated inductively or in a furnace. Byproducts and unused precursors are trapped (often cryogenically), neutralized and precipitated for disposal. The pump output is vented through a stack.

For metal coatings carbonyls and halides are commonly used:



Ceramics use similar types of reactions, e.g.



Diamond is also deposited by CVD by reactions such as



although ratios of reactants vary and the chemistry is poorly understood.

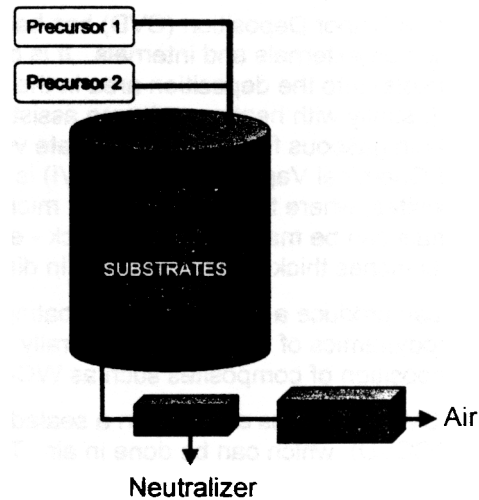
Note that in all these cases, which are typical of the CVD process, the precursors and/or the byproducts are corrosive, pyrophoric, flammable, or toxic (extremely so in the case of nickel carbonyl). Careful handling of materials and proper treatment of process exhaust is essential for worker safety and environmental protection.

The reaction temperature can be reduced by using more reactive species; e.g. the deposition temperature can be reduced to about 600C by using  $\text{TiCl} + \text{TiCl}_2 + \text{TiCl}_3$ , etc. formed in-situ by passing chlorine over hot  $\text{Ti}^{13}$ . **Because of the high processing temperatures thermal CVD is unsuitable for structural components**, although it can be (and frequently is) used for turbine blades and other hot section engine components.

### 9.2.2. Metal-organic CVD (MOCVD)

Many metal-organics are less stable than the halides, permitting the reaction to be run at much lower temperatures - typically 400 - 500C, although some reactions can take place only a little above room temperature. Precursors are typically alkyls and hydrides, such as triethylaluminum, arsine, and silane. Precursors must be either bought or synthesized for the correct reactions. They are often very expensive and difficult to handle.

The method is most heavily used in semiconductor and optical applications, where the mechanical strength and adhesion of the coating are not as critical as they are in wear. Because of cost and concern over mechanical performance MOCVD has not been used for making tribological coatings.



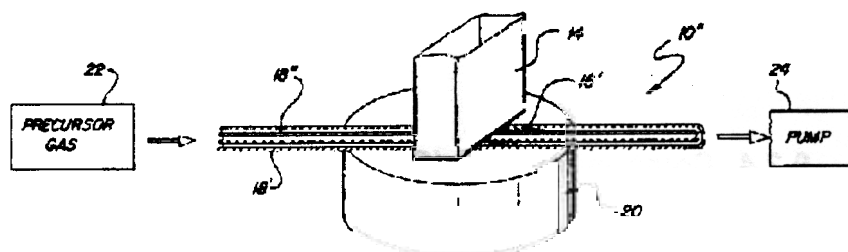
**Figure 21. Typical thermal CVD system.**

<sup>13</sup> Liburdi Engineering, Toronto, Canada

### 9.2.3. Plasma and Laser CVD (PCVD and LACVD)

Instead of heat, the reactions can be driven by other energy sources such as plasmas or lasers. The advantage of these approaches is that it is possible to maintain the bulk of the component at low temperature while heating only the surface region where the reaction occurs.

In LACVD the most common approach is to use the laser as a localized heat source to deposit material beneath the beam. In photo-laser CVD optical excitation is the driving mechanism<sup>14</sup>, which avoids substrate heating, but deposition rates are generally low. Plasma CVD is more widely used than laser CVD, especially for large substrates.



**Figure 22. Plasma CVD inside a tube, Energy Conversion Devices Patent # 5,223,308.**

A plasma CVD method has been patented by Energy Conversion Devices<sup>15</sup> for use in IDs (see Figure 22). This method uses microwave energy to excite a plasma within the tube and is claimed to be capable of depositing high quality coatings (such as optical quality SiO<sub>2</sub>) at temperatures of about 200C. However, since it depends on the tube being transparent to microwaves, it cannot be used for metal components, making it useless for structural aircraft parts. It would in principle be possible to create a microwave plasma by using the ID of the component itself as a waveguide, provided a standing wave pattern was not set up along the ID causing strong variations in plasma density (and hence coating thickness).

A large-area plasma CVD method is currently used commercially for the deposition of a clear, abrasion-resistant SiO<sub>2</sub> layer (trade name Vitrinite®) on such items as brass hardware, polymer sheet, and aluminum alloy wheels. The method is based on a technology developed by Dow Chemical<sup>16</sup>, and is done by Metrolite Surfaces, Inc. using tetramethyldisiloxane (TMDSO) liquid precursor that is vaporized into the chamber together with oxygen. The resulting material is not pure SiO<sub>2</sub>, but a less brittle material SiO<sub>1.8-2.4</sub> C<sub>0.3-1.0</sub> H<sub>0.7-4.0</sub>.

Vitrinite® coatings can be made as thick as about 2 mils, but could not be used for heavy rebuild. They offer good corrosion resistance and abrasion resistance to relatively soft materials such as brass and polymers, but they do not have the hardness of chrome or WC-Co. Note that most plasma CVD coatings are quite thin (one or two mils at most), making them more useful at the OEM than at the O&R level.

In this PCVD process there are multiple plasma sources throughout the chamber, which is typically 6' dia by 12' long. These sources create plasma throughout the chamber, from which the coating deposits onto the substrates. Clearly, a similar method could be used to create

<sup>14</sup> See, for example, A. Watanabe, M. Mukaida, Y. Imai, K. Osato, T. Kameyama, and K. Fukuda, J. Materials Sci., Vol.28, pp.5363-5368, (1993).

<sup>15</sup> US Patent #5,223,308, "Low temperature plasma enhanced CVD process within tubular members" Energy Conversion Devices (1993).

<sup>16</sup> Patent numbers 5,298,587 (1994); 5,320,875 (1994); 5,433,786 (1995); 5,494,712 (1996).

plasma inside a tube, using plasma sources such as post magnetrons, a single rf or dc biased electrode, or a pair of electrodes, or even a high-current electrode such as that used in the Surface Solutions PVD ID sputtering method.

Another major use of PCVD is diamond and diamond-like carbon (DLC) coating, using various combinations of methane, acetylene, hydrogen, and oxygen as precursors. Several companies sell microwave PCVD systems for this type of process<sup>17</sup>.

There are many ways of creating a plasma for PCVD, but the methods for ID coating must have plasma generators that fit inside the component. A plasma generator (such as an arc or high frequency probe) could be inserted into the ID to create a localized plasma, or an rf or dc rod electrode could be used to form a plasma along the entire length of the ID. Plasma can even be generated at atmospheric pressure using a corona discharge<sup>18</sup>.

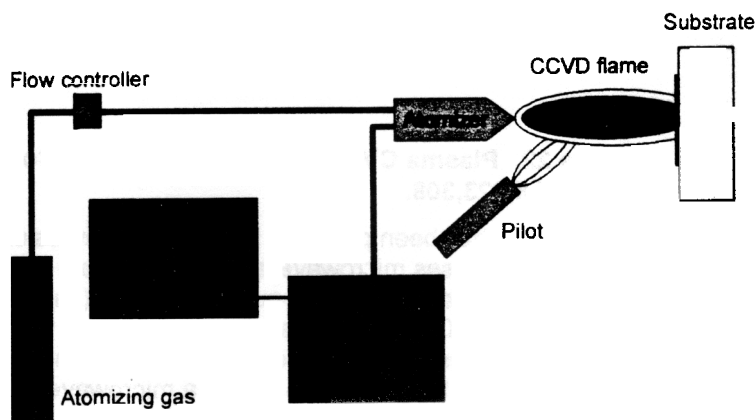
#### 9.2.4. Combustion CVD (CCVD)

Because of its high deposition temperature thermal CVD is unsuitable for most aerospace alloys. CCVD is similar to thermal spray, but the material being sprayed is in gaseous rather than powder form. For example, tetramethylsilane can be used for CCVD deposition of  $\text{SiO}_2$ <sup>18</sup>.

There have been one or two reports of doing CCVD using a flame spray or plasma spray gun. One variation on the method has been recently developed at Georgia Tech<sup>19</sup>.

The precursor material (which is the source of the metallic elements of the coating) is dissolved in a volatile organic solvent, which is pumped into an atomizer nozzle. When the resulting fuel is burned in air the precursor decomposes and the resulting compound (usually an oxide) deposits on the surface. Although oxides are obviously the easiest materials to deposit, nitrides and other compounds can be deposited under the correct reducing conditions.

In common with other CVD processes, CCVD is not line-of-sight and should therefore be capable of coating internals. Unlike other CVD processes, substrates can be held below 100C during deposition. The substrate generally needs to be either in the flame or not too far beyond it, but the temperature can be held down by moving the flame across the surface (or the surface across the flame) The method therefore avoids coefficient of thermal expansion (CTE) mismatch stresses, which arise in thermal CVD from the difference in thermal expansion as the temperature falls from the deposition temperature. However, internal coating stress is not known and is likely to be a limiting factor in coating thickness, especially for ceramic coatings, as is commonly the case with PVD ceramic coating methods.



**Figure 23. MicroCoatings Technologies' Combustion CVD.**

<sup>17</sup> For example, AsTex, Inc; Advanced Refractory Technologies

<sup>18</sup> Fraunhofer Institute, Braunschweig, Germany

<sup>19</sup> The main proponent of Combustion CVD is MicroCoating Technologies in Atlanta, who have exclusive rights to Patent # 5,652,021, owned by Georgia Tech, issued in July 1997.



### 9.3. State of development

**Thermal CVD** is a widely used commercial process, but its high process temperature makes it unsuitable for structural components.

**Metal-organic CVD** is in wide commercial use, but not for mechanical coatings where adhesion and mechanical strength are critical. Precursor cost and availability and safety concerns preclude its use in O&R.

**Plasma CVD** is commercially available for limited applications and materials. If the right coating material were used it could be a viable method, although coating thickness may not be enough for its use in O&R.

**Laser CVD** is still in the development stage and used mostly for semiconductor and optical applications. The Kansai Research Institute in Japan does offer laser CVD systems for commercial use.

**The CCVD process** is particularly interesting because of its simplicity and lack of dangerous precursors (although it does use volatile organics, which are burned in the process). It is currently under research and commercial development, and is being tested for a very wide range of coating materials and applications, including corrosion, wear, electrical insulation, fuel cells, catalysis, and high temperature superconductivity. MicroCoating Technologies has not attempted to carry out internal coating with the technique. There is therefore no data on how well it would work for this application, although we would expect the CVD technology to be quite effective for internals. At this point there is insufficient data to provide a clear decision on the suitability of the method for internal coating.

Although MicroCoating Technologies advertises the coating as a chrome replacement, there is no publicly available data that confirms its suitability for this purpose. Silica and alumina are usually somewhat harder than hard chrome (and therefore more abrasion resistant). The coatings appear to be considerably more corrosion resistant than chromate conversion coatings (on aluminum) or hard chrome. However, scratch-corrosion testing does not appear to have been done.

MicroCoating had completed a successful Phase I program and now has a Phase II SBIR program with the Navy (contract # N00014-97-C-0265, awarded in April 1997) for development of chromate conversion replacement and thermal oxidation resistant coatings. These coatings are based on silica and alumina<sup>20</sup>, although the company also has looked at mullite, YSZ, and chromia. Initial data shows that, as barrier coatings, silica and alumina have good high-temperature (800-900C) oxidation resistance and salt-fog corrosion resistance (1344 hours). No comparative data with chrome have been given (chrome would not be used at these high temperatures), and there is no indication of mechanical performance. The coatings are usually in the micron thickness range (from 10 nm to 5  $\mu$ m). We would not expect the method to produce good mechanical coatings several mils in thickness because typical oxide ceramic coatings are usually too highly stressed and too brittle, especially at high thickness. This would limit the use of the method to OEMs.

### 9.4. Coating materials and properties

The CVD method is extremely versatile in terms of the number of different materials that can be deposited. CVD works best for depositing simple compounds such as nitrides, carbides, and oxides (including mixed oxides, which are difficult to do by thermal CVD but can be done by CCVD) and metals such as Mo and Ni. Since it is done in air, CCVD is best at depositing oxides. Alloys cannot be deposited by CVD, although it is possible that the CCVD process may be able

<sup>20</sup> A. Hunt et. Al. "Thin film coatings for aircraft via CCVD processing", Proceedings - Aerospace/Airline Plating and Metal Finishing Forum, p 139-157, San Antonio (1998).

to deposit alloy chemistries but in amorphous or nanocrystalline form, probably with quite different properties than those of the bulk alloys.

High quality wear coatings (nitrides and carbides) are almost exclusively deposited by thermal CVD. There is little or no data on the properties or performance of wear materials produced other CVD methods. In general we should expect most plasma or combustion CVD coatings deposited at low temperatures to have relatively poor adhesion, just as PVD coatings have, unless the process involves scrupulous surface cleaning and ion bombardment. Laser CVD coatings could in principle be fused with the underlying material to produce a very good bond, but there is very little information available on the mechanical properties of such coating.

## 9.5. Capabilities

**Dimensions** - Thermal and MOCVD can be done in holes as small as a few microns in diameter and aspect ratios of greater than 100:1. PCVD is more limited by the need to create a plasma in the ID, and is likely to be limited to 0.5" or so in diameter, depending on the design of the plasma generator. Since CCVD has not been attempted in IDs there is no data on the subject, but it should be possible to coat IDs greater than about 0.5", since, unlike the thermal spray methods, the CCVD flame does not need to be aimed at the surface. (However, adhesion in these circumstances is questionable since the method would not provide energy directly to the surface.) LACVD could similarly coat small IDs, provided only that a mirror can be placed within the component.

**Coating materials** - Almost any metal or simple compound (nitride, oxide, or carbide) can be deposited, but the method is not suitable for alloys, composites, or complex compounds. CCVD may, however, be capable of depositing alloy chemistries by the simple expedient of dissolving more than one metal salt in the solvent, although this has not been demonstrated.

**Substrate materials** - Thermal CVD is limited to high temperature materials, such as turbine blade alloys, which can withstand 1,000C process temperatures. PCVD and CCVD are capable of very low process temperatures (as low as 100C), allowing them to be used on any structural material.

## 9.6. Limitations

**Precursors** - Many CVD precursors are toxic, flammable, pyrophoric, or highly acidic, posing serious potential hazards to personnel. While they can be handled safely in the controlled environments of semiconductor plants and CVD coating shops, they are not likely to be easily accepted for use in the much more diverse and open environment of DoD depots.

**Materials** - While CVD methods can deposit a very wide range of materials, the materials suitable for chrome replacement are much more limited. CVD methods cannot be used for depositing composites such as WC-Co, but they can be used for depositing hard metals or oxides and nitrides. However, the mechanical performance of hard coatings deposited by methods other than thermal CVD is as yet very poorly documented. The materials most easily deposited by CCVD are oxides, which are likely to pose severe problems for stripping, since most are impervious to all but the strongest acids.

**Equipment** - While there is commercial equipment available for thermal CVD, there is very little commercially available equipment for PCVD, LACVD, or CCVD. Metroline manufactures PCVD equipment specifically for Vitrinite® deposition. However, there appears to be no commercially available equipment for ID CVD deposition.

**Thickness** - Thermal CVD is used to fabricate bulk objects such as infrared windows. However, it is far from clear how thick potential chrome replacement coatings can be made when deposited by PCVD or CCVD. In most cases, other CVD methods are limited by internal stress or low deposition rates. For example, while thickness and rate data are difficult to obtain, practitioners of these processes consider 0.002" (PCVD) or even 0.0002" (CCVD) to be "thick". It

is likely, therefore, that these methods will be limited to OEM use, and will not be reasonable methods for O&R rebuilding.

### 9.7. Developments needed

A great deal of development would be needed to bring any of the CVD processes into use for ID coating of structural components. Developments need to focus on materials, processes, and equipment.

**Materials** - An adequate chrome replacement material needs to be defined that is compatible with safe, readily available, and inexpensive precursors as well as meeting the technical requirements for chrome replacement.

**Processes** - Processes must be developed that can be done both in small and large components, and can safely be used in both OEM and O&R environments. CCVD is probably the most likely candidate to achieve this aim since it does not entail flooding the component with precursor gas.

**Equipment** - ID coating equipment would need to be developed. Small CCVD torches do not seem to pose any serious difficulty. PCVD using a small plasma head operating with precursors injected through the plasma might also be a viable option. In both cases, the design would need to limit the use of precursors and attempt to ensure that virtually all the precursor material is consumed in the process, which will make the equipment much safer to operate.

### 9.8. Recommendations

Of the above methods, only a limited number are suitable for structural components, and fewer still are suitable for use in depot maintenance. As shown in Table 22, only PCVD and CCVD would appear to be potentially suitable for ID chrome replacement. Of these, CCVD appears to be the simplest, but it may also be the most limited in the materials it can deposit.

**Table 22. Summary of CVD suitability.**

| CVD technology  | OEM suitability | Depot suitability | Notes   |
|---|-----------------|-------------------|---|
| Thermal CVD   | No              | No                | High temperature.   |
| Plasma CVD  | Yes             | Yes               | No commercial processes or equipment for IDs. Significant development needed.   |
| Laser CVD   | Perhaps         | Perhaps           | No commercial processes or equipment for IDs. Significant development needed. Laser power and surface heating are concerns. |
| CCVD  | Yes             | Yes               | Needs significant testing and development.  |
| Note: All CVD methods require the right choice of coating material for performance and thickness, and attention to availability and safety of precursors. |                 |                   |   |

**Given the lack of development and lack of knowledge on these processes, we do not recommend them for ID coating at this time.** However, PCVD and CCVD might be viable OEM processes, although it is doubtful that they can be used for O&R.

## **10. Process Summary - Physical Vapor Deposition (PVD)**

### 10.1. Introduction

PVD is a vacuum process, usually, but not always, having a base pressure in the  $10^{-6}$  Torr region (high vacuum). In general the use of vacuum chambers imposes limitations on component sizes and requires the utmost cleanliness to prevent contamination.

We consider here only those methods that are designed for ID coating.

**Table 23. Summary information - PVD**

|                              |  |
|------------------------------|--|
| <b>Process name</b>          | Physical Vapor Deposition (PVD)  |
| <b>Description</b>           | Vacuum deposition from a solid or liquid source - typically sputter, arc, or evaporation |
| <b>Coating materials</b>     | Ta, nitrides and carbides (such as TiN, CrN)   |
| <b>Temperature</b>           | Typically 150 - 450C. Without active cooling temperatures would probably exceed 600C.    |
| <b>Minimum ID</b>            | Sputtering - 2", larger with blind holes. Plasma jet - less than ½"                      |
| <b>Maximum depth</b>         | None   |
| <b>Stage of development</b>  | Sputtering - commercial development (in test at Boeing). Plasma jet - research.          |
| <b>Primary advantages</b>    | Cleanliness, range of chemistries for different applications                             |
| <b>Primary disadvantages</b> | Vacuum process, cost, mostly thin coatings (thick coatings with limited chemistry)       |

### 10.2. Process description

PVD is the general name for a large number of vacuum processes that start with the coating material in a solid (or in rare cases a liquid) form, vaporize it, and deposit it onto the surface. The primary PVD methods are

- Evaporation - usually by electron beam or from a resistive boat (can be very fast)
- Arc - spark erosion of the deposition material (moderately fast, high ion bombardment, generally rougher surface)
- Sputtering - erosion of the deposition material by a plasma or ion beam (usually slow, but high quality).

While the principal PVD methods are variants of thermal evaporation, arc evaporation, and sputtering, there are many less widely used PVD methods, including

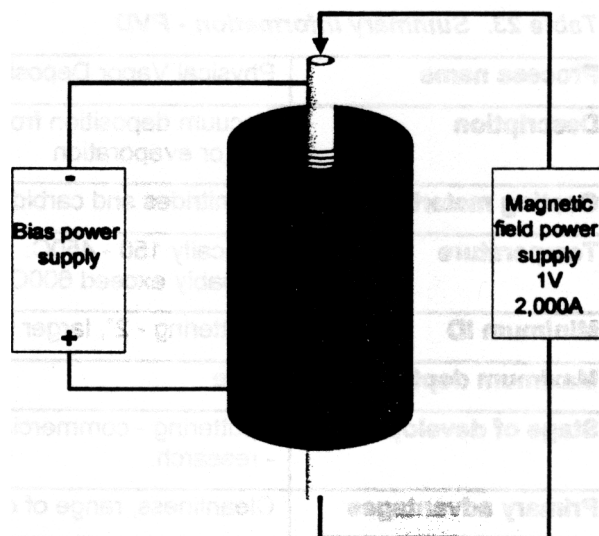
- Ion Beam Assisted (or Enhanced) Deposition (IBAD, IBED), which uses an ion beam instead of plasma bombardment
- Jet Vapor Deposition (metal vapor entrained in a high velocity gas stream),
- laser ablation (evaporation by laser pulses), and
- exploding wire (evaporation by a large current pulse in a thin wire).

Almost all PVD methods require ion bombardment, by a plasma or ion beam, both of the surface, to clean it atomically prior to coating, and of the growing coating, which otherwise tends to be weak and porous. In fact, inadequate or non-uniform ion bombardment is the most common cause of failure in PVD coating.

Most PVD methods are not suitable for use in IDs because they are essentially line-of-sight, with limited throwing power (i.e. ability to coat around corners and down holes).

### 10.2.1. ID sputtering

By its nature, PVD is inherently a line of sight method. The most advanced ID PVD method is the sputtering method developed by Surface Solutions, Inc., of Colorado, which is illustrated in *Figure 24*. Efficient sputtering requires a high plasma density in the vicinity of the material to be deposited (the cathode), which is achieved by the use of a magnetic field in a "magnetron" configuration. In the magnetron electrons follow corkscrew patterns around the magnetic field lines, ionizing the gas, which is usually held at a pressure of about 3 - 10 millitorr. The positive ions from the plasma are attracted to the target, which they hit at an energy of 500 - 1,000 eV, knocking (or sputtering) the surface atoms from the target.



**Figure 24. Schematic of Surface Solutions sputtering system.**

Most sputter magnetrons have permanent magnets to create the magnetic field. Since permanent magnets are generally rather bulky for ID coating, the approach adopted by Surface Solutions is to create the field by running a very high current (1,000 - 2,000 A) down a water-cooled cathode in the form of a hollow tube that is placed in the center of the hole. This current creates a circular magnetic field around the rod and sputtering occurs down its entire length, depositing material along the entire ID.

### 10.2.2. Plasma jet

An alternative method is under development in Sweden<sup>21</sup>. It consists of a small gas jet made of the material to be deposited, that can be biased to create a plasma that sputters material from the jet onto the walls of the tube. An entire ID could be coated by moving the jet along the axis of the hole. It would not be suitable for large areas, but is capable of coating very small diameters. This method is in the research stage, and is far less developed than the Surface Solutions method, and for that reason, we shall not consider it further here.

<sup>21</sup> See, for example, H. Barankova, L. Bardos, and S. Berg, *J. Electrochem. Soc.*, **142**, 883 (1995); H. Barankova, L. Bardos, T. Nyberg, and S. Berg, *J. Electrochem. Soc.*, **141**, 375 (1994)

### 10.2.3. Exploding wire

Another PVD process that would seem ideally suited to coating the insides of tubes is exploding wire technology. The method consists of passing a fast high-voltage (5-10 kV), high current pulse through a thin wire in the center of a tube (usually by discharging a high-voltage capacitor through it). Over a period of a few microseconds the wire melts and the vapor ionizes in the electric field, forming an intense plasma and a rapidly-expanding sheath of vapor and small droplets that expand to the wall and coat the tube ID.

Exploding wires have historically been used for fundamental plasma studies or for igniting some of the older high-power lasers. In the 1980's there was a brief flurry of activity in evaluating the method for coating, but it disappeared and has never surfaced as a coating process.

Grabatin et al<sup>22</sup> actually used the process for deposition of Ta coatings onto 20mm ID, 70 mm long gun tubes to a thickness of about 0.004" by exploding a single 1mm diameter wire. The coating performance appeared quite good.

Since this time, however, the process seems to have disappeared from the literature, and is not being offered commercially.



Figure 25.  
Exploding wire.

### 10.2.4. High rate chrome deposition by PVD

Since the primary problem with chrome plate is not the chrome itself, but the hexavalent air emissions, an alternative to chrome plating is PVD coating. (This does not, of course, address the problem of stripping solution disposal.) A number of companies have developed PVD chrome alternatives. For example, Implant Sciences of Wakefield, MA has developed a high rate arc deposition process capable of depositing at rates  $>1\mu\text{m}/\text{min}$  ( $>0.002"/\text{hr}$ ). Preliminary data show that the material was about 25% softer than hard chrome (588 K<sub>N</sub>H, vs 766 K<sub>N</sub>H for hard chrome), but performed much better in pin-on-disc wear tests in hydraulic lubricant. At this point, however, the method uses a planar arc source that is capable only of deposition on externals, and the deposition equipment would have to be re-engineered in order to use it for ID coating.

There are methods for arc deposition inside a tube. Wedtech Corp. has a patent for arc-evaporating material onto the inside of a tube by spiraling the arc along an internal electrode<sup>23</sup>. The method is shown in Figure 26, which is drawn from the patent. An arc struck by a movable electrode spirals along it, depositing coating inside the tube. How well this works in practice, however, is not known since Wedtech Corp no longer exists and the method is not in commercial use.

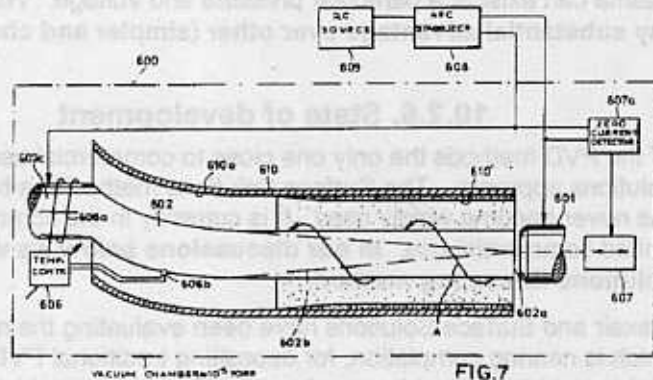
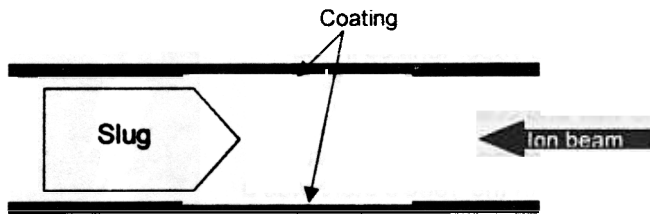


Figure 26. Wedtech spiral arc coating of tube ID - US Patent #4.609.564.

<sup>22</sup> H. Grabatin, V. Schlett, H. Stuke, and H. Weiss, *J. Vac. Sci. Tech.* A3, 2545 (1985).

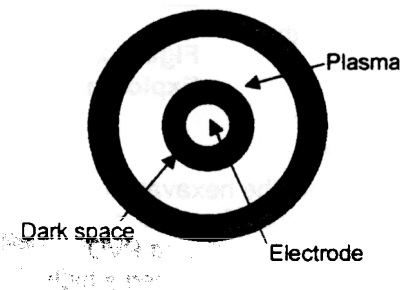
<sup>23</sup> US Patent # 4609564, "Method of and apparatus for the coating of a substrate with material electrically transformed into a vapor phase", Wedtech Corp., inventor Eduard Pinkhasov (1986).

### 10.2.5. Ion beam assisted deposition (IBAD, IBED)



**Figure 27. Possible proposed ion beam coating of ID.**

sputter a conical "slug" inside a tube to get around the line-of-sight restriction (Figure 27), but have found that sputter rates are far too slow for cost-effective deposition.



**Figure 28. Possible proposed PSII arrangement.**

Another proposed approach has been to use variants of the plasma source (or plasma immersion) ion implantation method (PSII, PI<sup>3</sup>). This approach uses a plasma as the source of ions, pulse-biasing the substrate (in this case, the tube) to effect ion bombardment (Figure 28). This approach can be thought of as a high voltage variation of the Surface Solutions method outlined in Section 10.2.1, but without the 1,000A DC magnetron current. Proposed methods have involved ideas such as alternately biasing a central rod negative and positive to create alternating bombardment of the rod (to sputter a coating) and the tube ID (to irradiate the coating). This method will only work at quite high pressures since the method relies on a plasma outside the dark field

(cathode fall region). This region around a high voltage electrode increases with voltage and decreases with increasing pressure, posing a lower limit on the diameter of tube in which a plasma can exist at a particular pressure and voltage. **This method does not appear to offer any substantial advantage over other (simpler and cheaper) sputter methods.**

### 10.2.6. State of development

Of the PVD methods the only one close to commercial use for ID coating is the Surface Solutions approach. The Surface Solutions method has been in existence for some time, but has never become widely used. It is currently in the commercial development stage, with some limited commercial use. **In our discussions below we will assume the use of the Surface Solutions ID coating method.**

Praxair and Surface Solutions have been evaluating the method under a NIST ATP program, which is nearing completion, for depositing traditional PVD coatings such as TiN. Because the final report has not yet been submitted, Praxair has not been willing to discuss the results. However, they say that they have been able to improve adhesion and coating quality, presumably by increasing ion bombardment of the ID wall. The report for this program should be released in the next few months.

In the Green Gun Barrel Project, the Army's Benet Lab is developing its own version of the Surface Solutions approach, which is in the development-demonstration stage. The Benet work has been supported by a SERDP program, which has now ended. A vertical coating system has been built, and has made a few test runs on gun barrels, but test firing results so far have not been very good (albeit better than other alternatives tested). The primary problem appears to be inadequate ion bombardment of the ID, both for plasma cleaning prior to coating, and for



establishing a high quality coating during the deposition process itself. The method is also very slow - about 24 hours for a 3 mil coating.

Boeing Defense is just beginning tests of an ID coating addition made to an existing IVD coater. While IVD has proved to be a viable commercial replacement for cadmium, the line of sight IVD process is incapable of coating IDs. In mid-1998 Surface Solutions delivered to Boeing St Louis equipment for depositing Al onto IDs, which is currently under test.

### 10.2.7. Coating materials and properties

For gun barrels, which are subject to extreme high temperature pulses and high velocity particle erosion, there is evidence that electroplated tantalum is a great improvement over hard chrome. Unfortunately Ta must be deposited by a salt bath method that is difficult and also has severe environmental problems. Benet Labs also wanted a coating that would be smooth enough to require no finishing after deposition. For these reasons they opted for sputtered Ta. **It is important to note that, while gun barrels and hydraulics are both chrome plated, their wear mechanisms are entirely different, meaning that the optimum coating materials for these two different applications will almost certainly be very different.** Sputtered Ta may or may not be comparable to chrome in wear resistance, as may Mo (which is thermal sprayed on piston rings for wear), W, Zr, or, of course, vacuum Cr. Tests would be needed to evaluate their relative wear properties.

- In general, the traditional PVD coatings such as TiN and CrN have been used for aerospace wear applications<sup>24</sup>, and in some cases for chrome replacement, but not in IDs.
- More lubricious materials such as DLC have shown more promise for hydraulics<sup>25</sup>. In this case the most critical issue is seal wear.
- The Japanese piston ring company, Taikoku, has developed, and sells commercially, a piston ring with a 60µm thick CrN/O arc coating in place of chrome plate. The coating takes several hours of deposition and must be highly polished after deposition. It is consequently very expensive.

Clearly, from *Table 24* and *Table 25* far more is known at present about the properties of traditional PVD coatings, and there is little solid information on PVD metals such as Cr and Ta. There is almost no information on the properties of ID Cr and Ta, meaning that if they are to be considered as chrome alternatives, a great deal of fundamental evaluation will be required. Of course, the method is not limited to elements or simple compounds. It could be used to deposit wear resistant alloys such as Hastelloys, Inconels, or Triballoys. However, knowledge of their properties is practically non-existent for PVD coatings, although there is a significant amount of data for plasma sprayed coatings of these materials. Because the sputtering process takes the material apart atom by atom and reassembles it at the substrate, it can reproduce the chemistry, but in general it does not reproduce the microstructure of the bulk material. Therefore the properties of PVD alloys may be quite different from those of the bulk materials.

<sup>24</sup> GE Aircraft Engines, Sundstrand Aerospace, for example

<sup>25</sup> "Evaluation of chrome rod alternative coatings", Report #GTE0598 (1997).

**Table 24. Materials properties - typical wear-resistant PVD coatings (nitrides)**

| Property                     | Value  | Notes   |
|------------------------------|--|---|
| Materials                    | TiN, ZrN, TiC, TiAlN, TiCN, BN, DLC, CrN, Cr | Most materials are nitrides or carbides of transition metals  |
| Hardness                     | 1200 - 2400 HVN                              | Depends on material and internal stress   |
| Maximum thickness            | 15 $\mu$ m                                   | Usually limited to about 5 $\mu$ m  |
| Corrosion resistance         | Moderate                                     | Limited by pinholes   |
| Wear resistance              | Excellent                                    | Better than chrome, comparable to thermal sprays. Note that wear <u>life</u> can be low because thickness is small.                       |
| Lubricity                    | A little less lubricious than chrome         | DLC and BN are particularly lubricious  |
| Porosity                     | <1%  | Pinholes are primary problem  |
| Stress and effect on fatigue | Strongly thickness-dependent                 | PVD coatings generally have very high compressive stress. Fatigue is usually adversely affected at coating thickness above a few microns. |
| Hydrogen embrittlement       | None   |   |

**Table 25. Typical materials properties - PVD Cr and Ta coatings**

| Property                     | Value - Cr                                | Value - Ta                                       | Notes  |
|------------------------------|---|--|--|
| Hardness                     | 588 KnH                                   | Unknown  | Can be increased by N incorporation  |
| Maximum thickness            | Unknown                                   | >0.003"  | Several mils are probably possible with both materials                           |
| Corrosion resistance         | Similar to hard EHC                       | Moderate   | NaCl solution tests  |
| Wear resistance              | Pin-on-disc better than EHC (approx 1/10) | Unknown. Hot erosion is critical for gun barrels | Wear rate is very sensitive to conditions. Data on in-service wear not available |
| Lubricity                    | Unknown                                   | Unknown  |  |
| Porosity                     | Unknown                                   | Unknown  | Depends on deposition method. Expect pinhole corrosion                           |
| Stress and effect on fatigue | Probably compressive                      | Probably compressive                             | Most thick PVD coatings reduce fatigue life                                      |
| Hydrogen embrittlement       | None                                      | None   |  |

### 10.3. Capabilities

**Dimensions** - IDs as small as 1" can be coated, and in a vertical system the item could be several feet long.

**Coating materials** - Almost any metal, alloy, or simple compound (nitride or carbide) can be sputter deposited, with varying rate and cost depending on the material.

**Substrate materials** - In principle the method is not limited by substrate. In practice, heat sensitive alloys are likely to be tempered unless heat can be removed efficiently from the ID surface through the wall.

**Equipment** - It appears to be possible for ID coating systems to be incorporated into existing IVD units. However, they will require additional jiggling, fixturing, and feedthroughs.

### 10.4. Limitations

**Thickness** - The primary limitation of PVD coatings is their thickness. The Ta gun barrel coatings are unique in their thickness. In most cases (especially for the more wear resistant ceramic coatings such as TiN and TiC) PVD coatings are deposited with quite a high compressive stress as a result of ion bombardment during coating. This stress builds as the thickness grows, until at some point it causes delamination. As a result PVD coatings are typically about 3  $\mu\text{m}$  thick, and seldom more than 15  $\mu\text{m}$  (about 0.0005"), with Praxair being the only aerospace PVD vendor we are aware of capable of offering these coatings in the 15 - 20  $\mu\text{m}$  range. The only PVD compound coating with a thickness of several mils is CrN/O used on piston rings. As a result of thickness and cost limitations, PVD coatings are generally useless for rebuilding worn components, which usually require thicknesses of 0.003-0.010".

Because they are less brittle and can be deposited more easily at a higher rate, metals can be realistically deposited at greater thicknesses than PVD ceramics. Ta coatings several mils thick can be used in gun barrels because Ta, being a metal, has a high fracture toughness compared with typical ceramic coatings, and we would expect that the lack of ion bombardment of the substrate during coating limits the compressive stress. (This is also the situation for commercial IVD aluminum, which can be deposited in thick layers.) We would expect a similar situation for PVD Cr and for PVD Mo (which is presently arc or plasma sprayed for replacing chrome on piston rings and some other automotive components).

**Vacuum** - The requirement for vacuum deposition imposes limitations on the size of items that can be processed, as well as the types of items that can be coated. For example, complex parts with slots and holes that act as reservoirs for oils and grease can be extremely difficult to coat reliably. Most vacuum chambers are a meter or so in size, although IVDs are several feet in diameter and long enough to accommodate even most landing gear parts. The need for vacuum does tend to raise the cost of most PVD processes, and requires properly-trained technicians.

**Deposition rate** - The sputtering process is one of the slowest PVD coating methods, with a rate of a few microns per hour. A gun barrel can be coated in about 24 hours. The deposition rate for hard ceramic coatings is frequently much lower than that for metals (depending on how process control is effected), and often drops to about a micron per hour. Combined with the high capital cost of PVD equipment, these long deposition times lead to very high costs for thick PVD ceramics, even where they can be deposited without flaking and delamination due to high internal stress.

The deposition rate for metals can be far higher - according to Implant Sciences, Cr can be arc deposited at more than a micron per minute.

**Temperature** - Most hard coatings require a substrate temperature from 150C to 450C, and in general the lower the deposition temperature, the less reliable the process. The lower range of temperatures is not a problem for most chromed components, but the upper range would be unacceptable for most aluminum alloys and high strength steels.

**Blind holes** - Because the method requires access to both ends of the cathode rod, the Surface Solutions method cannot presently be used to coat blind holes. Surface Solutions is working on a new design to overcome this limitation, but it is currently only in the concept stage. It will doubtless be larger in diameter than the existing system because of the need to bring the current down and back, presumably with magnetic shielding or a dipole arrangement to prevent the opposing currents neutralizing the magnetic field.

### 10.5. Fit with OEMs and depots

**Thickness** - Because of the thickness limitation for hard PVD coatings, the fit with depot maintenance is poor. PVD coatings can be (and are) used for chrome replacement by OEMs, especially on components that are high tolerance and that never need to be rebuilt (e.g. engine components that are typically replaced rather than rebuilt). However, **the inability to rebuild worn components makes PVD hard coating of no real value for hard chrome replacement in the O&R environment.**

**Vacuum** - The complexity of vacuum equipment does not generally fit well with depot maintenance shops. It is very different from most other depot rebuilding and coating operations, which are predominantly involved with machining, welding, thermal spray, and bath deposition. However, with the replacement of cadmium plating by IVD aluminum, IVD (a vacuum PVD process) is now in use at a number of depots, and the depots are building up experience with operating this type of vacuum equipment. The equipment used for IVD aluminum is not typical of that used for hard coatings, which is generally more complex. On the other hand, there have been efforts in DoD to extend the capabilities of this type of equipment to hard coatings. **In principle, it may well be possible to incorporate ID PVD into existing IVD chambers, and ensure a better fit with depot operations.** This principle is being tested at Boeing-St. Louis for depositing IVD aluminum onto component IDs. If it is successful at Boeing, the equipment may be installed at Ogden ALC.

**Material** - One very favorable aspect of PVD is that the method can be used for rapid deposition of chrome. At this point high rate chrome deposition has not been demonstrated for ID coating, but there is no reason in principle that it should not be possible. It would presumably be easier to obtain approval for PVD chrome because of its similarity to electroplated chrome. **This approach would eliminate air emissions, but would not eliminate chrome stripping and grinding wastes** (although grinding is likely to be minimal for smooth PVD coatings).

### 10.6. Typical costs and cost factors

In PVD coating, cost is directly related to deposition rate. Labor is the primary cost factor, with capital equipment depreciation a close second in most cost models. Materials tend to be a rather small fraction of the total cost. However, as the coating thickness grows, materials costs become increasingly important. The Surface Solutions method requires a hollow tube of tantalum, chromium, or other less-common metal. The cost of these types of materials can be high and availability can be a problem. They should, however, be easier to obtain than the large flat plates typically used in planar magnetrons. At present there are no data available on production costs with ID magnetrons. However, there are various cost models for standard PVD coatings.

For example, Implant Sciences estimates a production cost of \$0.22 /in<sup>2</sup> for a 1 mil Cr coating on simple cylinders, which works out to be about 20% greater than hard chrome plating. This estimate takes into account normal business costs and actual coating costs, but does not include

pretreatment (where we would expect PVD to cost a little more because of the need for more careful cleaning), or post-treatment such as hydrogen embrittlement anneals (which raise the cost of hard chrome) and grinding.

For work we have previously done under DARPA funding, we estimated costs for chrome plating versus PVD and thermal spray methods. A 3 $\mu$ m CrN coating on piston rings (again a very simple geometry with no hydrogen embrittlement relief needed even for chrome plate) had a cost of about \$0.55 /in<sup>2</sup> as against about \$0.80 for chrome plate. In this case finishing (grinding) was about 30% of the cost for hard chrome, but only 5% for PVD coating - an unusual situation. When a 15 $\mu$ m CrN PVD coating was used (which Cummins Diesel considered would be necessary to attain the same wear life as the 3 mil chrome plate), the cost was estimated at about \$1.70/in<sup>2</sup>.

### 10.7. Developments needed

**Thickness** - At the OEM level, thin coatings are perfectly acceptable, provided that the wear life (wear rate x thickness) is adequate. To be of value in the O&R environment, rebuild thicknesses will be needed, requiring deposition rates of at least a mil per hour (about 10 times current hard coating rates). At the same time methods must be devised to ensure that these very thick PVD coatings have little internal stress.

**Cleaning and ion bombardment** - This is a critical issue. PVD coatings do not work unless the surface is scrupulously clean. First, chemical cleaning is required using aqueous cleaners. Present aqueous cleaning systems for PVD usually involve high pressure liquid jets, which cannot be used effectively on tube IDs.

Secondly, the surface must be atomically cleaned by ion bombardment in vacuum immediately prior to deposition. With the present geometry, it has proved very difficult to adequately ion clean the substrate or ion-irradiate the growing coating, both of which are crucial to proper adhesion and hardness. In standard PVD coating these issues are handled quite easily. However, in a closed tube surface oxides must be removed without redepositing them elsewhere, and there must be sufficient plasma density at the tube wall for effective ion bombardment of the growing coating.

Watervliet has not yet found a way to do this, but Praxair seems to have come up with methods that improve the coating quality, presumably involving some measure of solution to these ion bombardment problems. The solution to this problem must be made generally available as part of the deposition system.

**Materials and performance** - For OEM use, the standard (thin) nitrides and carbides are likely to be the most useful. However, for O&R use, thicker coatings of metals such as Cr, Ta, or Mo (which can be deposited much more rapidly with less internal stress) or perhaps of hard alloys such as Hastelloy or Tribaloy, appear to be the only viable options. Extensive testing and performance measurement will be needed to be sure of the adequacy of these coating materials. Note that the mere fact that an alloy such as Hastelloy is used as the cathode merely ensures that the coating will have similar chemistry. It does not ensure that it has similar properties, since the properties of most alloys depend on their microstructure, which is likely to be completely different in the coating from the bulk alloy. (PVD is a non-equilibrium process whereas alloy manufacture is an equilibrium thermodynamic process.)

**Equipment and process** - Vacuum deposition equipment will need to be made simple to operate, with built-in process menus. The most viable approach for O&R depots would seem to be to install ID hard coating equipment into existing IVD chambers, which are large and which the depots already know how to operate.

**Surface preparation and finishing** - Machining and cleaning of the tube ID are critical to proper PVD coating adhesion - much more than any other type of coating. Unfortunately most cleaning systems currently used for PVD processing are made for bath-cleaning and spraying ODs, but

are not well-designed for ID treatment. Production PVD coating will require careful attention to the design of new methods to ensure proper cleaning of IDs.

PVD coatings are generally considered to be very smooth and therefore to need no further finishing. This is true for typical thin coatings. However, as coatings become thicker, differences in grain growth rates tend to make some crystallographic orientations grow at the expense of others, coarsening the surface. Proper grinding methods will need to be developed for PVD coatings.

## 10.8. Recommendations

PVD coating technology appears to be a niche product for IDs, best suited to high-value OEM products. Traditional PVD hard coatings are not suitable for O&R use since they cannot be grown thick enough due to stress and cost limitations. Metallic PVD coatings, such as Cr, Ta, Mo, and hard alloys, may be viable for rebuilding IDs. Unlike the nitrides the metals can be deposited to higher thickness without excessive stress, and metal deposition is relatively simple.

However there are several issues that will need to be addressed:

- **Deposition methods and equipment** - Although the equipment exists to sputter deposit metals on IDs, many of the details of the process require development, especially ion cleaning and ion bombardment, both of which are critical to the PVD process. Equipment will need to be redesigned for use in blind holes. We believe that the best approach would be to adapt the Surface Solutions method to existing IVD chambers.
- **Performance** - Performance of the materials that can be used for rebuilding in typical ID applications is unknown (and likely to be inferior to the traditional hard nitrides). In this regard, Cr deposition holds the least risk, since it is basically the same material as that which it replaces. However, microstructure is clearly going to be different, and details of the chemistry may be changed as well. Furthermore, of course, PVD Cr does not eliminate stripping and grinding wastes.
- **Cleaning** - this is a critical issue for IDs. While important for any coating method is especially crucial for PVD coatings. Typical aqueous parts washing and precleaning, which work well on ODs, will have to be adapted to IDs.

Overall, PVD coating could meet many of the OEM and O&R requirements for ID coating. While the limitations of vacuum processing would make it difficult to do on the IDs of large components, it may be a viable method for chrome replacement on medium to small component IDs.

## **11. Process Summary - Laser Processing**

## 11.1. Introduction

Laser processing breaks down into three main techniques:

- Laser cladding, in which a solid (powder, wire, etc.) is fused onto the surface
- Laser CVD (in which material is deposited from the gas phase)
- Laser alloying (in which material is integrated with the underlying surface)
- Laser surface modification (in which the laser beam is used to glaze or "peen" the material without introducing additional elements).

While the latter two items may be of value to OEMs, in common with heat treatments, they are not of value to O&R operations since they cannot be used for rebuild. In fact, however, the methods are somewhat indistinct, since the difference between cladding and alloying, for example, is primarily determined by the power and length of the laser pulse.

Laser methods are becoming more industrially viable as lasers have improved dramatically in the past few years, with the production of high power Nd-YAG, CO<sub>2</sub>, and even diode lasers, that are robust and designed for industrial use. Furthermore laser integrators can now design and produce entire laser systems for cutting, engraving, and materials modification.

**Table 26. Summary information - laser processing.**

| Process name                 | Laser coating  | Laser alloying  | Laser modification                                       |
|------------------------------|--|---|--|
| <b>Description</b>           | CVD or PVD addition, primarily welding                             | Surface melting and alloying of material on surface   | Glazing or "peening" by direct laser-surface interaction |
| <b>Coating materials</b>     | Metals and alloys  | Not a coating - limited build-up                      | None   |
| <b>Temperature</b>           | >500C  | Melt temperature                                      | Peening - low<br>Glazin - melt                           |
| <b>Minimum ID</b>            | Depends on method  | Depends on method                                     | Depends on method  |
| <b>Maximum depth</b>         | Unlimited  | Unlimited   | Unlimited  |
| <b>Stage of development</b>  | Niche production   | Development   | Development and niche production                         |
| <b>Primary advantages</b>    | Simple heat source<br>Moderate capital cost<br>Excellent adhesion  | Excellent adhesion (not a coating)<br>Gradable alloys | Reduced porosity (glazing)<br>Low temperature (peening)  |
| <b>Primary disadvantages</b> | Easy to overheat surface (fatigue concern)<br>Not suitable for O&R | Not suitable for build-up                             | Not suitable for build-up                                |



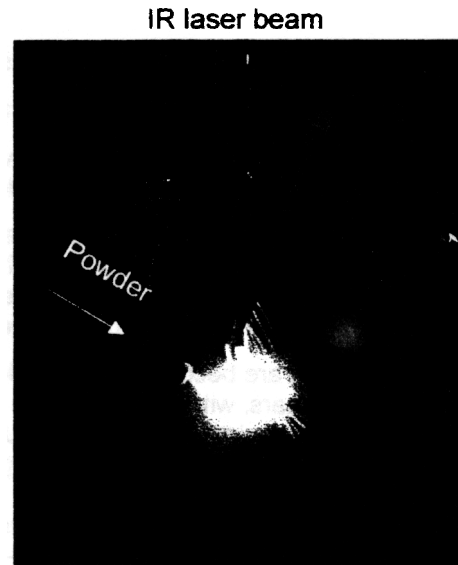
## 11.2. Process description

### 11.2.1. Laser cladding

Laser cladding is the general name for a method of coating in which coating material is brought to the surface (usually in powder or wire form) and melted (or welded) onto the substrate using a high power laser such as a Nd-YAG or CO<sub>2</sub>. Figure 29 shows a powder-fed cladding system. The powder is fed from an angle above, and the laser comes from directly above (hence the heating of powder particles bounced or expelled upwards into the beam).

Laser cladding requires sufficient surface heating to weld the materials together, which means that the surface heat treat is modified by the process, leaving a heat-affected zone beneath the coating. The coating tends to be very rough, with a "ploughed field" effect of raised strips of weld material. Instability in the powder feed can leave gaps in the coating with excessively heated surface beneath.

Laser cladding tends to be used for high temperature material. For example, GE Aircraft Engines uses the method for coating the tips of some hot section turbine blades. It is not easy to set up the correct processing parameters, but once they are determined the method can be very reliable.

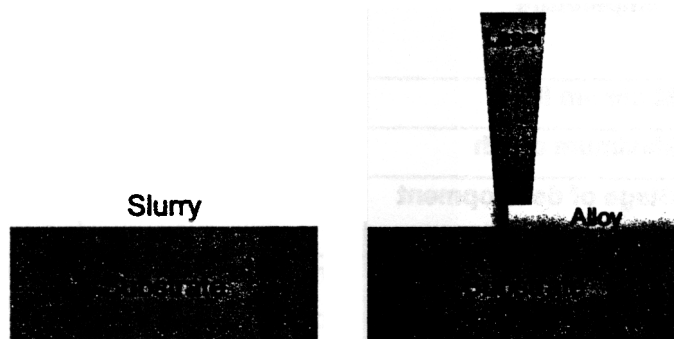


**Figure 29. Powder-fed laser cladding process.**

### 11.2.2. Laser Induced Surface Improvement (LISI)

The University of Tennessee has developed a surface alloying method that they call Laser Induced Surface Improvement (LISI). The material to be alloyed is incorporated into a light-absorbing slurry that is painted or sprayed onto the surface. A high power laser is then used to burn off the organic material and create a short-lived surface melt pool that alloys the material into the substrate to form a surface alloy.

While the method adds some material to the surface, it is really an alloying process rather than a coating process, and as such cannot be used for rebuild



**Figure 30. LISI schematic. Slurry-coated surface (left) is laser alloyed (right).**

### **11.2.3. QQC Diamond**

QQC Diamond has been heavily marketed over the past two or three years. It is basically a modified laser CVD technique involving the use of three laser beams<sup>26</sup> that is proprietary to QQC Corp. The details of the process are not understood, but it is believed that one laser aimed at the substrate vaporizes carbon-containing material and redeposits it as diamond, while another deposits carbon from the ambient hydrocarbon gas, and the diamond-like material produced diffusion bonds to the substrate. The method is proprietary and would be complicated to use for IDs. Furthermore, diamond coatings, while they may be very good for OEM use, cannot be used for rebuild. **Therefore we will not consider this approach further.**

### **11.2.4. Laser glazing and peening**

Laser glazing consists of using the beam to remelt the surface, which rapidly solidifies into a thin, smooth "glaze". This layer is usually hard and amorphous, so that it improves corrosion resistance by eliminating through porosity. Both metals and ceramics can be glazed, and it is a method that seems to be quite successful on thermal spray coatings.

A laser "peening" method has been introduced in which water is flowed across the surface and a high power pulsed laser fired into it creates intense shock waves that peen the surface.

Neither of these methods is suitable as a chrome replacement since neither creates any build-up.

### **11.2.5. State of development**

Laser cladding is used in production for niche applications such as turbine blades, but is not available as a standard job shop process or as standard equipment.

The LISI process was developed at the University of Tennessee and is being offered by Surface Treatment Technologies, Inc. of Tennessee, who are commercializing the process. It is still early in the development cycle and is probably ready for niche applications. Limited data is available on performance.

The QQC diamond process is being offered commercially by both QQC of Michigan and by QQC West in Nevada, but its main application appears to be golf club heads, and for most other applications it is still in the development stage.

### **11.2.6. Coating materials and properties**

Laser cladding can be used for a wide variety of metal and alloy coatings. Since it is a weld technique it cannot readily be used for ceramics, although it is perhaps possible that ceramic particles might be melted in the surface.

## **11.3. Capabilities and advantages**

**Laser cladding** - The method can be used to weld into the surface any compatible alloy that can be delivered in wire or powder form. In general the method requires reasonable access for the laser beam and the feed material, with the laser striking the surface at roughly normal incidence. For IDs this would require the laser to be brought down a tube with a mirror at the end, or a reflective light guide. The weld material would be most easily delivered as a wire, but could be delivered in powder form just as it would be for ID thermal spray.

Because it is a weld, coating adhesion is excellent.

<sup>26</sup> US Patent # 5,731,046: Fabrication of diamond and diamond-like carbon coatings. Also US Patent #s 5,643,641, 5,635,243, 5,620,754.

**LISI** - The process is intended to be a surface alloying method. However, it is possible to vary the laser power and pulse duration to limit diffusion so as to form anything from a fully formed, uniform alloy to an alloy with a high surface concentration of the alloying material. Enough power must be supplied to ensure bonding at the interface, which means that essentially the whole slurry must be melted.

Since the slurry is applied prior to laser processing, the difficulties of slurry delivery are largely avoided. All that is required is that the slurry be uniformly distributed across the surface.

## Limitations

### Laser cladding:

- Because it is a weld process it involves substantial surface heating and the formation of a heat-affected zone at the surface, raising serious concerns of overheating and fatigue.
- Laser cladding was tested during a previous DARPA contract<sup>27</sup> that helped to decide the direction of the HCAT. It was found to be too dangerous for general use because of the likelihood of overheating, especially if the material feed was interrupted. The process window between welding and alloying at the surface was too narrow for reliable operation on diverse components. The weld material often cracked during multiple passes because of stresses from repeated high heat and cool cycles. **Therefore the method was not recommended for depot use.**

### LISI:

As an alloying process the method involves substantial surface heating, or even melting. This raises serious concerns over the heat-affected surface layer and its effect upon fatigue.

Although some material is added, it alloys with the surface and does not form a build-up layer. Substantial build-up might be possible by adding sufficient material, but that is not the way the process is designed, and it would involve a great deal of surface heating.

As with all laser systems, ID coating would require a mirror inside the ID close to the wall where deposition or alloying is taking place. The system would need to be designed to ensure that the mirror did not become contaminated either with metal or burned off hydrocarbon. For IDs this is a much more serious problem than it is for ODs where the laser can be placed further away from the surface being processed.

## Fit with OEMs and depots

### Laser cladding:

Laser cladding fits well with very specific applications and components in production. However, in general these are best chosen to be high temperature materials, or components that can be reheat-treated after cladding. The method is not suitable for O&R use since it is too easy to damage components by overheating.

### LISI:

The technique is similar to laser cladding, but with the primary differences that it is an alloying method rather than a coating technique and that the alloying material is applied to the surface prior to laser treating. This is an advantage in preventing heat damage, which can occur in laser cladding when the powder or wire delivery is momentarily interrupted.

<sup>27</sup> Final Report Grant #MDA972-93-1-0006 "Hard Chrome Coatings: Advanced Technology for Waste Elimination", PIs Keith Legg and George Nichols (1997).

Since it does not add significant dimensions to the surface it is not suitable as an O&R method.

#### **QQC Diamond:**

As we have noted above, the QQC Diamond method is not suitable either for OEM or O&R chrome replacement on IDs.

### **11.6. Developments needed**

Laser coating methods are becoming increasingly viable as industrial processes, primarily because of the widespread development of reliable laser equipment for the metalworking industry - primarily for cutting and boring. However, at the present time laser methods cannot be used as general coating methods since there are several basic issues that must be either developed or evaluated if either of the above laser methods (or methods of similar type) are to be used:

1. Measurements of the effect on component performance of the surface heat-affected zone - It is assumed that disturbance of the existing heat treat will make this zone into a poorly-defined weak point, possibly initiating cracks and early fatigue. This effect is likely to vary from one material to another, and it is quite possible that in the high strength steels used in most ID applications, the effect will be to improve fatigue performance if compressive stress is created in the surface alloy.
2. Feedback control to prevent overheating - Modern lasers are stable, but heat input to the surface can vary depending on the instantaneous particle of wire feed rate (cladding) and the local slurry thickness (LISI). Sensing and feedback control would prevent damage to heat-sensitive structural components. However, doing this for IDs will be considerably more difficult than for ODs where access is relatively easy.
3. Understanding the limitations of multiple passes, which currently can result in cracking of the coating, presumably due to differential thermal expansion in the rapid heat-cool cycles.
4. Development of ID coating methods - There are some equipment problems peculiar to ID coating that need to be solved, including introducing both the beam and the coating material, and ensuring that internal optics do not become coated or damaged during the process.

### **11.7. Recommendations**

**At this point we do not recommend laser processing for ID chrome replacement.**

However, the future promise of laser processing is bright enough that it would be worth first evaluating item 1 in Section 11.6 above to determine if there are inherent problems for these methods on aircraft components, before proceeding to any further development.

## **12. Process Summary Weld Coating**

## 12.1. Introduction

Weld coating has been used for many years for hard-facing large items such as agricultural equipment. In that case the weld is a very thick coating laid down from a weld rod, with concomitant extreme surface heating. There are much finer methods now available to deposit thin coatings with little substrate heating or to weld a surface layer directly onto the underlying material. Of these there are two that are particularly useful for IDs:

- Electro-spark deposition, which is a form of micro-arc welding using a consumable electrode
- Explosive bonding (cladding), in which a thin surface layer is attached across the entire surface by use of an explosive charge.

**Table 27. Summary information -**

| Process name                 | Electrospark Deposition  | Explosive Cladding  |
|------------------------------|--|---|
| <b>Description</b>           | Micro-arc weld facing  | Metallurgical joining by explosively driving materials together |
| <b>Coating materials</b>     | Metals (inc. W alloys, Cr, Ta alloys, Stellite, Tribaloy, MCrAlY); cermets with Ni or Co (inc. WC, Cr <sub>3</sub> C <sub>2</sub> , TaC) | Formable metals; some ceramic powders                           |
| <b>Temperature</b>           | < 100C bulk, local surface melt; heat-affected zone < 1mil deep  | <100 C bulk; unknown local temperature during cladding          |
| <b>Minimum ID</b>            | 0.3"   | ~1"   |
| <b>Maximum depth</b>         | None   | None  |
| <b>Stage of development</b>  | Limited commercial; validation needed for aerospace  | Early commercial; developmental for aerospace                   |
| <b>Primary advantages</b>    | Low capital cost<br>Simplicity<br>Very small areas - no masking  | Very thick repair<br>Low capital cost                           |
| <b>Primary disadvantages</b> | Small areas only<br>WC-Co thickness limited  | Operator training/safety - not suitable for general use         |

## 12.2. Process description

### 12.2.1. Micro-arc welding (Electrospark deposition, ESD)

The electrospark deposition method has been in existence for more than 10 years. It is essentially a miniature consumable-electrode TIG arc welding method in which a small DC arc transfers electrode material from the cathodic electrode to the workpiece, laying down  $1\mu\text{m}$  or less on each pass. Almost any electrically conductive material can be deposited in this manner.

ESD is offered by several small companies, including

1. Advanced Surfaces and Processes (ASAP) in Oregon (PulsFusion™ alloying)
2. Turbine Metal Technology in California
3. JIT Automation in Ontario, Canada

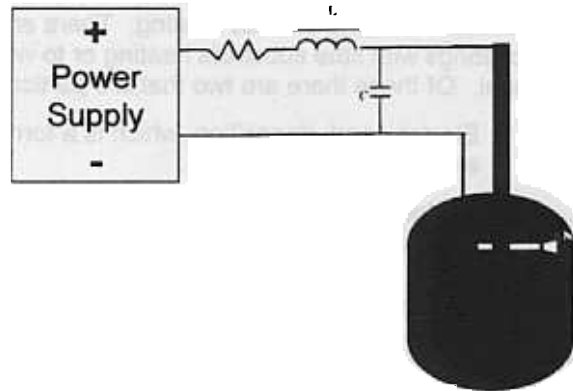


Figure 31. Electrospark deposition (ESD).

The primary non-commercial researcher in the technology is Roger Johnson of Battelle Northwest.

Because the electrode can be made very small, the method is capable of depositing coatings deeply into very small IDs (as small as  $\frac{1}{4}$ "). Any material that is conductive and can be made into an electrode can be deposited, but with differing efficiencies and thicknesses.

Because it is a weld overlay, the coating creates a thin heat-affected zone at the substrate surface (Figure 32). The coating itself is fine-grained or essentially amorphous because it is rapidly solidified from an extremely small melt pool after each arc. Arcs occur at a frequency of 10 - 1,000 Hz and each arc lasts about 1 - 10  $\mu\text{sec}$ . The electrode remains essentially in contact with the surface so that each arc is highly localized.

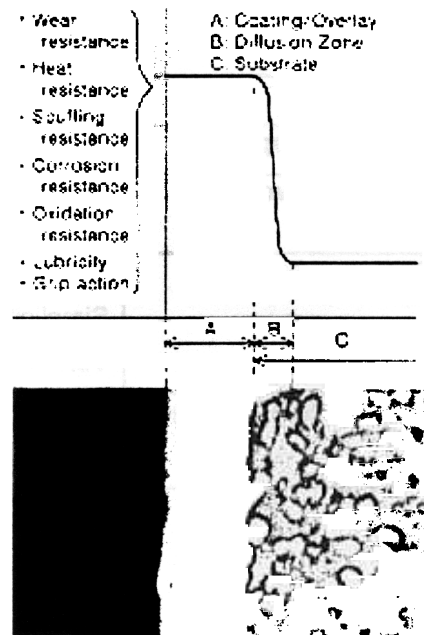
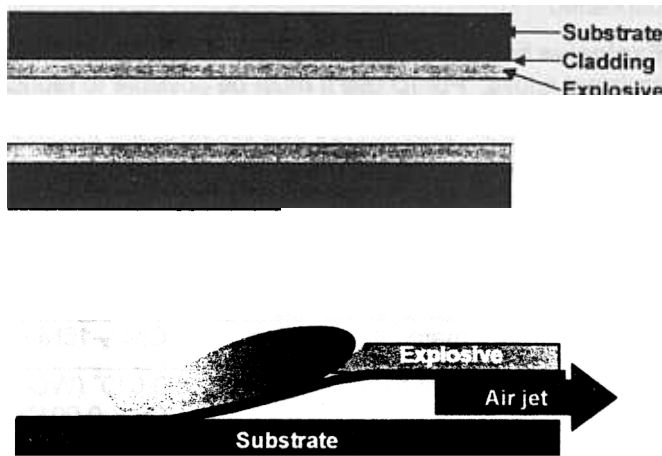


Figure 32. Cross-sectional detail of EDS coating (Technocoat, Japan).

### 12.2.2. Explosive bonding (cladding)

Explosive cladding has been used for many years. It consists of putting the materials to be bonded in close proximity and driving them together with explosives (Figure 33). A high bond strength is achieved kinetically, rather than by heating, making it a cold process. In fact the belief is that as the explosive burns and drives the two surfaces together, a powerful jet of air is forced out from between them, cleaning the surfaces to permit a strong metallurgical bond (Figure 33, below).

For internals the method would consist of making a thin "can", which would fit within the ID to be clad, and driving it into the component with a small explosive charge.



**Figure 33. Explosive bonding. Above - tube ID cladding set-up. Below - explosion detail.**

The advantage of the method is that, since it does not involve heating, it can be used to join dissimilar materials such as aluminum and copper. The dynamics of the process usually creates a wave structure at the interface that in cross-section looks like saw teeth. Sigtabond Technologies, of Ontario, Canada claims to have found a way to make the interface smooth.

Obviously, with this process care must be taken to ensure that the component is capable of withstanding the shock of the explosion.

### 12.2.3. State of development

ESD is a commercial process, and is used successfully for a number of applications, including

- sodium valves in sodium-cooled nuclear reactors
- nuclear reactor pump IDs for liquid lithium
- power turbine blade notch surfaces
- power turbine blade tip coatings for diffusion/oxidation/corrosion resistance

Although the process is developed, there is limited information on how it would affect the properties of aerospace components. Therefore, for the purposes of applying it to the IDs of aircraft components, such as hydraulics, we must consider the applications still to be in the developmental stage.

Explosive cladding, in the form in which it could be applied to aircraft parts, is still very new. While the process has been brought to limited commercial use there are many unknowns in the process and its effect on components.

## 12.3. Coating materials and properties

Both of these methods are capable of depositing many different types of materials.

**ESD** - The coating and substrate materials must both be electrically conductive. Some alloy coatings can be made very thick (especially Ni alloys), but some materials, such as WC-Co are self-limited to about 0.001" because they begin to spark-erode equally on both electrode and coating when this thickness is exceeded. One of the most successful wear-resistant ESD



coatings is chrome carbide in a Ni binder. Wear resistant alloys, such as Stellite, can also be deposited.

**Explosive bonding** - The easiest materials to join are metals, including steels and wear-resistant alloys. For ID use it must be possible to fabricate the metal "can" to the shape of the ID. It is possible to use the method to clad with metal or ceramic powder. In this case the explosion rapidly compresses and solidifies the powder into a solid. The porosity of the resulting material is unknown.

**Table 28. Typical materials properties - ESD and Explosive Cladding**

| Property                     | ESD                                  | Explosive Cladding                         |
|------------------------------|--------------------------------------|--|
| Hard material examples       | Cr <sub>3</sub> C <sub>2</sub> -15Ni | Stellite, tungsten                         |
| Maximum thickness            | 0.010" (WC-Co < 0.001")              | >.250"                                     |
| Corrosion resistance         | Good                                 | -  |
| Wear resistance              | Good                                 | -  |
| Porosity                     | Low                                  | ≤ bulk metal alloys;<br>ceramics - unknown |
| Stress and effect on fatigue | Not known                            | Not known                                  |
| Hydrogen embrittlement       | None                                 | None                                       |

## 12.4. Capabilities

**ESD** - The method can be used in very small, long IDs. The only requirement is that a small electrode can be inserted into the component. Its advantages are:

- simplicity and low capital cost
- excellent adhesion - since it is a metallurgical weld
- low deposition temperature - since each arc is low power and short, heating is only at the surface
- ability to coat very small diameters (~0.5") and long lengths (10 feet)
- wide range of coating materials.

**Explosive cladding** - The method cannot be used for very small IDs, but could work well on any simple ID, without complex shapes such as ring grooves. The cladding material must be conformable to the shape of the surface being coated. Its advantages are:

- joining of any two materials, including thermodynamically immiscible metals
- good metallurgical bond
- very thick rebuild coating.

## 12.5. Limitations

**ESD** - Its disadvantages are:

- cannot be used for large areas (too slow and expensive)

- cannot be used for small ring grooves whose dimensions are similar to or smaller than the electrodes
- possible fatigue debit resulting from heat-affected zone at the surface
- cracking of the coating has been observed, and there is likely to be tensile stress at the surface due to coefficient of thermal expansion (CTE) mismatch - both potential fatigue and corrosion problems
- less-conductive coating materials such as WC-Co are self-limiting to about 0.001" thick
- the surface of the coating is rough, which is a particular concern for replacing thin dense chrome on IDs.

The most serious concern for aerospace companies who have examined the method (such as Orenda) is cracking of the coating and a possible fatigue debit due to modification of the microstructure of the component.

The small size of the electrode poses inherent component size and coating thickness limitations, which are likely to severely restrict its application in O&R and in components such as landing gear. We expect it only to be viable for small areas such as hydraulic actuator IDs, lugs, pins, etc., but not for large areas such as landing gear IDs.

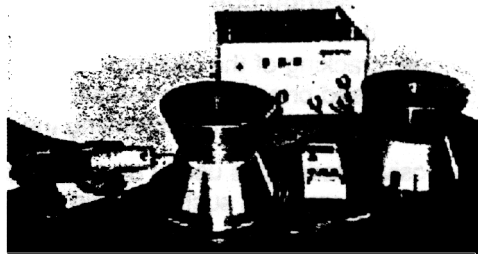
**Explosive cladding** - has the following disadvantages:

- only usable for simple shapes
- component must be able to withstand the mechanical shock
- safety issues inherent in explosives use - would probably have to be supplied as "repair packs" with measured amount of explosive and clad preform.

The primary concerns are again with the effect of the process on fatigue. There is also likely to be concern over any possible effects such as sub-surface crack growth, and institutional concerns of operator training and safety.

## 12.6. Fit with OEMs and depots

ESD would fit easily into both the OEM and depot environments. The equipment is small and simple to operate. Figure 34 shows the power supply (rear), and the electrode (left), with two steel roller guides to which the coating is being applied. The electrode for the unit shown in Figure 34 is hand-held, but for consistency it would need to be robotic. This has been done for coating nuclear reactor components.



**Figure 34. ESD unit (Technocoat, Japan).**

The fit of explosive cladding is less easy to gauge. It is best used for depositing layers some mils thick, either of hard-facing material at the OEM or of build-up material at the O&R site. In fact, on simple components it might be an excellent method of obtaining a very thick build layer. It could not be used as a general repair technology, however, due to operator safety and liability issues. Sigabond has suggested that they could supply repair kits comprising a properly sized and shaped "can" of cladding material together with the correct amount and form of explosive. At this point, however, we would see it as a method to be applied by the vendor rather than by the OEM or depot.

## 12.7. Typical costs and cost factors

For ESD the primary cost factors are area (which translates directly into coating time) and coating material (since different materials coat at different rates, with simple metals such as Ni being fast and materials such as WC-Co being slow and/or self-limiting). A typical coating rate is about 3 sq. in./minute for a 2 mil WC-Co coating, at a typical cost of about \$5 - \$7 per sq. in. This means that a hydraulic actuator, for example, that is 1.25" ID and 8" long would take about 10 minutes to coat at a cost of about \$200. On the other hand a landing gear 8" diameter and 48" long would take about 7 hours to coat at a cost of about \$7,000 - far higher than either chrome plating or thermal spray.

## 12.8. Developments needed

**ESD** - The primary developments that are needed are evaluating coating properties and the performance of coated components. The primary issue is the nature and thickness of the heat-affected layer and the effect it might have on fatigue and ultimate tensile strength. Other coating issues such as CTE mismatch and cracking of the coating are also serious concerns.

For ID coating chrome replacement it would be ideal to be able to use WC-Co, just as is now being done on ODs with HVOF. This will require the real cause of the limit to be determined, and overcome if possible. If that cannot be done, a good alternative will need to be found that offers similar performance (i.e. better than chrome).

For replacement of thin dense chrome on IDs, the ESD coating would need to be ground to achieve the proper rms surface finish. A method of automatic deposition that would minimize or eliminate this requirement would be very useful.

**Explosive cladding** - The effects of the process on both substrates and components will need to be evaluated carefully. Since its most likely use is as a repair on specific components, or for hard-facing specific OEM items, it will need to be evaluated and validated for those specific niche applications.

## 12.9. Recommendations

**The ESD method could be a good answer for ID coating of small components, such as pins, hydraulic actuators, lugs, etc.** Since there are serious questions as to the effect on fatigue, cracking of the coatings, and surface stress on the component, these questions should be addressed prior to any evaluation on components themselves. Methods for depositing smooth coatings and for increasing the thickness of coatings such as WC-Co need to be found.

Explosive cladding is useful as a niche product for certain difficult OEM hard-facing or O&R thick repair problems. As such it should be evaluated on a case-by-case basis only.

### **13. Process Summary - Heat treating and Ion Implantation**

### 13.1. Introduction

Heat treating methods are currently being used to replace chrome plating on items such as hydraulic piston ODs, and many could equally well be used on IDs. They are valid methods for improving the wear and corrosion resistance of alloys, and as such make a great deal of sense for OEMs. **However, heat treating techniques are not suitable for depot rebuilding, since they do not add any material to the substrate.** We have included ion implantation in this section since it has many similarities to traditional heat treating, especially in that it modifies the existing material surface rather than adding a coating to it.

**Table 29. Summary information - Heat treating and ion implantation**

| Process name                 | Heat treating  | Ion implantation   |
|------------------------------|--|--|
| <b>Description</b>           | Plasma or gas nitriding, carburizing, nitrocarburizing, etc.   | Injection of ions from a beam or, in case of PSII, from a plasma |
| <b>Coating materials</b>     | None   | None   |
| <b>Temperature</b>           | 500 - 800C   | < 200C   |
| <b>Minimum ID</b>            | None for gas nitriding, 1" for plasma nitriding  | Probably >3" (PSII only)   |
| <b>Maximum depth</b>         | Unlimited  | Unlimited (PSII)   |
| <b>Stage of development</b>  | Commercial   | Research, development  |
| <b>Primary advantages</b>    | Large scale commercial process<br>Can be done at OEM stage<br>In use for OD hydraulic chrome replacement | Low temperature  |
| <b>Primary disadvantages</b> | Cannot be used for rebuild<br>High temperature   | Cannot be used for rebuild                                       |

## 13.2. Process description

### 13.2.1. Heat treating

There are a number of heat treating methods that might be considered potentially useful for ID treatments **at the OEM level only**, including

- gas nitriding,
- gas carburizing,
- gas nitrocarburizing,
- plasma nitriding,
- plasma source ion implantation.

The gas nitriding, carburizing, and nitrocarburizing treatments involve heat treating in an enclosed furnace at a temperature of 500 - 1,000C for about 12 hours in an atmosphere containing active gases ( $N_2$ ,  $NH_4$ ,  $CH_4$ ,  $H_2$ , etc.). The result is diffusion and formation of nitrides, carbides, etc. with nitride- and carbide-forming alloying elements to a case depth of up to 0.060". Most steel gears, for example, are carburized. Because they are gas processes these methods treat the entire surface, including IDs. In fact, any surface that is not to be treated must be copper plated and the copper stripped at the end of the treatment.

The plasma processes utilize a combination of heat and plasma bombardment to carry out similar heat treatment, and consequently can often be done at lower temperature. Plasma nitriding, for example, is usually done at a temperature of 500 - 520C and a pressure of 1 - 10 Torr, giving a case depth of 0.005 - 0.025". The plasma processes are generally cleaner and better controlled than the gas methods (especially when pulsed rather than DC power is used). Because plasma is easy to shield, the plasma methods do not require copper plate on areas that are not to be nitrided. The plasma methods can be done in IDs provided care is taken to ensure plasma penetration without forming excessive hollow cathode plasma densities, which can cause extreme heating and erosion.

The gas and plasma heat treating processes are sometimes combined with gas or plasma oxidation to produce an outer oxide layer that provides better corrosion protection. Several companies offer this type of process commercially.

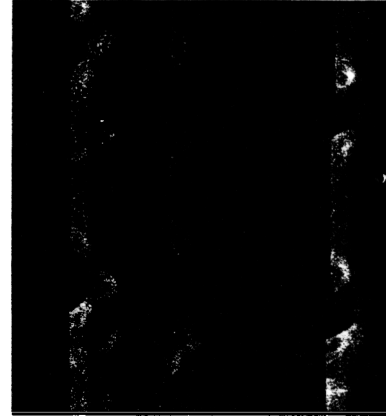
### 13.2.2. Ion implantation

Plasma source (or immersion) ion implantation (PSII or PI<sup>3</sup>) can be thought of as a high voltage form of plasma nitriding, in which the temperature is kept very low. There has been some debate, in fact, over the extent of surface heating and plasma nitriding that can take place in PSII, since some workers have reported nitrogen diffusion profiles. Provided the temperature is kept low, however, the method affects only the outermost few tenths of a micron.

Note that beam line implantation (which uses an ion beam instead of a plasma) is wholly unsuitable for IDs since an ion beam is strictly line-of-sight and cannot be fired into the wall of an ID except at grazing incidence.

### 13.2.3. State of development

The gas and plasma heat treating techniques are fully commercial processes that have been in the market for many years (although the plasma processes are more heavily used in Europe



**Figure 35. Plasma nitriding.**  
(Note bright plasma with dark space next to surface.)

than in the US). Full scale commercial equipment is readily available for both gas and plasma processes.

Standard hydraulic rod heat treated by the Nitrotec™ nitrocarburizing process is available commercially as a replacement for traditional chrome plated rod.

The PSII process has been under development for a number of years and is in limited commercial use. One or two companies offer production equipment for the process<sup>28</sup>, and it has been offered commercially<sup>29</sup> as a way of producing more wear-resistant chrome.

### 13.3. Capabilities

The primary use of these heat treatments is for steels rather than for aluminum alloys, although the method is now being tested for aluminum alloys<sup>30</sup>. The gas treating processes work very well on both ODs and IDs. While the plasma processes work on IDs, care must be taken to ensure that the ID is properly bathed in plasma. Depending on the pressure, the hole diameter, and other factors the ID can have no ion bombardment for lack of plasma penetration, or it can be excessively bombarded (with consequent etching and overheating) by formation of hollow cathode plasmas.

### 13.4. Limitations

**Materials** - Because of the temperatures involved, these gas and plasma processes must be properly integrated into the heat treatment for the original component. Because the surface of the material is modified, the performance is strongly materials-dependent.

**ID treatment** - Beam line implantation cannot be used for ID treating. PSII could be used if the ID were large enough to contain the anode and the dark space around it, with an adequate amount of plasma for bombardment.

**O&R use** - Since these methods do not add material **they are of no value for component rebuilding**. Furthermore, the treatments must often be followed by further heat treating to return the component to its proper heat-treated state. This is not true for PSII, provided the process is controlled to keep the part temperature low.

### 13.5. Fit with OEMs and depots

Gas or plasma surface nitriding, etc. is a relatively simple fit with OEM products, since OEM components and steels are heat treated in any case, and the additional processing could well be incorporated as part of that treatment. However, it is of no value for O&R since it cannot rebuild worn components.

One should also consider carefully how the adoption of such a heat treat might affect subsequent O&R processes. Coating processes that lock onto the surface physically, such as thermal sprays, should not be affected by an underlying treatment. However, it is known that PVD coatings adhere very poorly to some heat treated surfaces, especially to carburized surfaces, and the same may be true of other processes (including electro- and electroless plates) that depend on a chemical bond.

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<sup>28</sup> For example, North Star Research Corp

<sup>29</sup> Empire Hard Chrome, Chicago. The company appears no longer to be offering the PSII process (at least as a standard chrome treatment).

<sup>30</sup> H.R. Stock, C. Jarms, F. Seidel, and J.E. Doring, Surface and Coatings Technology 94-95, 247-254 (1997).

### **13.6. Typical costs and cost factors**

Heat treating processes such as gas or plasma carburizing and nitriding are relatively inexpensive since components can usually be treated in batches in very large furnaces (often 6' or more in diameter, and 6 - 20' high). For typical industrial products pricing is by the pound, from \$1.50/lb for small items to \$0.60/lb for large items weighing several thousand pounds.

Following the heat treat the surface must usually be descaled and may require grinding to remove the hard, brittle "white layer" and to bring the surface back to permissible Ra values. Quality assurance is an additional major part of the cost for aerospace components, and usually involves hardness testing and hardness depth profiling on coupons made during the heat treatment.

After treatment, most materials must be further heat treated to bring the bulk properties back to their original heat treating specifications.

### **13.7. Developments needed**

With the exception of PSII, all the treatments are commercial and need only be adapted to each material and component geometry.

Because there has been little use of these treatments on aluminum, work would be needed to develop proper process parameters for aluminum alloys. In common with all other processes, extensive data gathering will be needed to ensure that performance and producibility criteria are met.

### **13.8. Recommendations**

Gas or plasma nitriding, carburizing, or nitrocarburizing are useful technologies that could be adopted for IDs. As we have already noted, nitriding, carburizing, etc. are only of value at the OEM level because

- they cannot be used for rebuild
- standard vacuum or air heat treatments will usually be needed to bring the components back to specified hardness and strength, which is relatively straightforward when part of the manufacturing process, but more difficult to do at the O&R level.

However, if these treatments were to be adopted at the OEM level, it would be critical to ensure that they do not make it difficult to overcoat at the O&R level. (Note that the heat treated surfaces cannot be stripped, so that if the surface has to be removed for coating, it can only be done by grinding.)

Since heat treating is fairly simple when done by the OEM, we do not believe that PSII offers any significant improvement over traditional plasma nitriding for IDs, except in circumstances where warpage is a significant problem. (Note that implanted surfaces are less likely to pose any problem with subsequent coating at the O&R level. This is, in fact, one of the selling points of ion implantation in plastics molds.)